The Kinetics and Mechanism of Ring Opening of Radicals containing the Cyclobutylcarbinyl System

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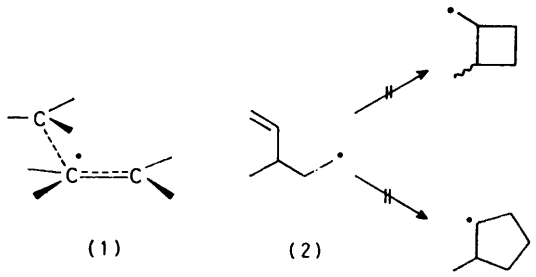
The kinetic parameters for β-fission of radicals containing the cyclobutylcarbinyl system have been determined by analysis of the mixtures obtained when suitable chloro-compounds are treated with tributylstannane. Under these conditions ring opening is irreversible and in the rigid bicyclic system (4) is under stereoelectronic control. For ring opening of cyclobutylcarbinyl radical (8) $k_f = 4.3 \times 10^3$ s^{-1} at 60°, and the best values of the activation parameters appear to be $\Delta H^{\ddagger} = 12.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7.4$ cal mol^{-1} K^{-1}. Monocyclic systems undergo preferential fission of the more substituted βγ-bond. Methyl substituents at the α-, β-, or δ-positions have little effect but γ-substitution strongly enhances the rate of ring opening. The transition state is reactant-like and has a similar disposition of centres to that (1) for homolytic addition.

PREVIOUS kinetic studies [1-10] of the cyclization of hex-5-enyl radical and related species have elucidated many of the intimate mechanistic features of intramolecular addition in free radicals. In particular, the propensity of suitably constituted alkenyl radicals to undergo *exo*-cyclization and the consequent recognition of the importance of stereoelectronic factors [1-3] strongly support the model (1) of the transition state recently advanced on theoretical grounds.[11] Other significant results have included the recognition that alkyl substituents at the seat of attack strongly retard the reaction,[4] and the observation that 1-methylhex-5-enyl and related species undergo cyclization preferentially in the *cis*-mode,[5] possibly because of the demands of orbital symmetry.

Cyclizations of hex-5-enyl and higher alkenyl radicals are usually irreversible.[6] On the other hand, the consequent relief of ring strain normally ensures that cyclopropylcarbinyl and cyclobutylcarbinyl radicals undergo ready ring opening by β-scission processes which are formally the reverse of intramolecular homolytic addition.[12] The rate constant for cyclopropylcarbinyl fission [13] is marginally too high to allow accurate kinetic measurements to be made by the tin hydride method, but the cyclobutylcarbinyl system is readily accessible.[14-16] Accordingly, a study of the reactions of various cyclobutylcarbinyl chlorides with tributylstannane was initiated with the following aims: (i) to verify the irreversibility of ring opening in simple cyclobutylcarbinyl systems; (ii) to determine whether this reaction, like β-scission of cyclopropylcarbinyl radical,[17] is sensitive to stereoelectronic factors; and (iii) to investigate the effects of alkyl substituents on the rate and regioselectivity of the reaction.

Irreversibility of Ring Opening.—Substantial evidence already exists that ring opening of the parent cyclobutylcarbinyl radical is irreversible. Pent-4-enyl radical has been generated under various conditions, but under no circumstances could any derivative of cyclobutane or cyclopentane be detected.[18] Because of the favourable effect of alkyl substituents on radical cyclization rates,[19] 3-methylpent-4-enyl radical (2) might be expected to undergo ring closure. However, when it was generated in the presence of tributylstannane at very low concentration (0.005M) no trace of methylcyclopentane, 1,2-dimethylcyclobutane, or hex-1-ene (arising *via* consecutive ring closure and opening) could be detected. The conditions of the experiment were such that 2% of rearrangement product was detectable, and we can therefore deduce that the value of the rate constant for ring closure of the radical (2) at 80° $\leqslant$ 250 s^{-1}. In experiments conducted concurrently with these [20] Davies and Pereyre [16] reached similar conclusions.

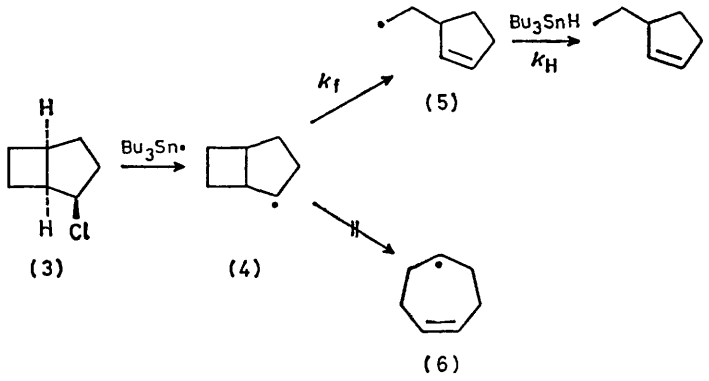


(1) (2)

In a further test of irreversibility the radical (5) when generated under various conditions of temperature and stannane concentration failed to afford cyclized products. Finally, the constancy of relative rate parameters for cyclization calculated for a variety of substituted cyclobutylcarbinyl radicals generated over a five-fold range of stannane concentration (see below) is consistent only with irreversible ring opening. We conclude that ring opening of the cyclobutylcarbinyl system is generally irreversible, and that ring closure of pent-4-enyl systems will be observed only when the cyclized form is especially stabilised by substituents.[21]

Stereoelectronic Effects.—Thermodynamic calculations [22] indicate the enthalpy of formation of the cyclohept-5-enyl radical (6) to be *ca.* 2 kcal mol^{-1} less than that of the isomeric radical (5). Therefore, the bicyclo[3.2.0]hept-2-yl radical (4) on β-fission, in the absence of any stereoelectronic effect, should behave analogously to related monocyclic radicals (see below) and afford preferentially the more stable product radical (6). In fact, treatment of the pure *endo*-chloride (3)

with tributylstannane in decalin afforded only bicyclo[3.2.0]heptane and 3-ethylcyclopentene. Under conditions capable of revealing the formation of cycloheptene in 0.1% yield it could not be detected. Clearly the bicyclic radical (4) undergoes regiospecific ring opening by the less exothermic route to afford the less stable product (5). The relative rate constant, k_f/k_H, had values of 0.25 and 0.42 mol l^{-1} at 80 and 91° respectively. These values are somewhat larger than those for the opening of an analogous monocyclic secondary radical [reaction (B2)] to give a *cis*-olefin, presumably because of the relief of strain associated with the bicyclic system.



The regiospecific ring opening of the bicyclic system (4) to give the less-stable possible product (5) is consistent with the view [1] that β-fission requires efficient overlap between the semi-occupied orbital and the σ (or σ*) orbital of the bond to be broken. Since the semi-occupied orbital in the radical (4) lies in a plane orthogonal to that of the internal cyclobutane bond, the stereoelectronic requirements for the formation of the secondary radical (6) cannot be met without considerable strain being generated in the transition state.

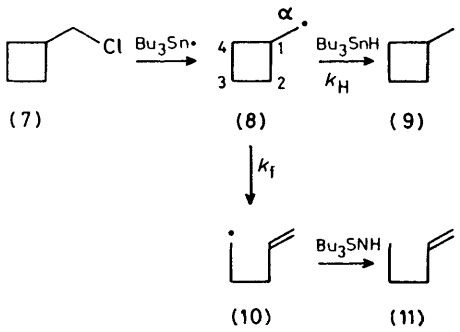
Similar results have been recently reported [15] for ring opening of the radical (4) generated from a mixture of *endo*- and *exo*-2-bromocyclo[3.2.0]heptane. Comparison of the two sets of results confirms that the rate and mode of ring-opening of the bicyclic radical (4) is independent of the nature and stereochemistry of the halogen in the radical precursor.

β-Fission of the Cyclobutylcarbinyl Radicals.—The kinetic data presented in Table 1 were obtained by analysis of the products formed by reduction of the appropriate cyclobutylcarbinyl chlorides with tributylstannane. The reaction pathway given for the parent compound (7) is equally applicable to the other chlorides. Since the bimolecular transfer of a hydrogen atom from stannane to the cyclobutylcarbinyl radical (8) competes with unimolecular formation of the acyclic radical (10) the relative yields of cyclic and ring-opened products (9) and (11) are related to stannane concentration, and the value of k_f/k_H can be determined by application of the appropriate integrated rate equation.[6] For those radicals possessing a plane of symmetry through the C(α)–C(1) bond, k_f/k_H has been halved to give the values per bond undergoing fission.

Since k_H is believed to be relatively independent of the nature of the alkyl radical, values of k_f/k_H for all the primary and secondary radicals studied can be directly compared to give values of k_{rel}, the rate constant for ring opening relative to that of the parent For tertiary radicals k_H is somewhat smaller [23] and values of k_{rel} have been adjusted accordingly.

Determination of absolute values for k_f requires a knowledge of the absolute kinetic parameters for the hydrogen atom transfer step. The value of k_H for abstraction by a primary radical has been determined [23] at 25°, but the Arrhenius parameters must be obtained indirectly from the known values of k_c and k_c/k_H for cyclization of the hex-5-enyl radical. Two sets of data giving k_c are available;[24,25] when combined with values [26] of k_c/k_H they give: $\log k_H = 8.3—3.1/2.3RT$; $k_H = 1.05 \times 10^6$ l mol^{-1} s^{-1} at 25°; 1.84×10^6 l mol^{-1} s^{-1} at 60° or $\log k_H = 9.5 - 4.8/2.3RT$; $k_H = 9.5 \times 10^5$ l mol^{-1} s^{-1} at 25°; 2.23×10^6 l mol^{-1} s^{-1} at 60°.

The first set of data, which should be the more accurate,[24] when combined with the present results for ring opening of cyclobutylcarbinyl radical gives: $\log k_f = 11.65 - 12.2/2.3RT$; $\Delta S^{\ddagger} = -7.44$ cal mol^{-1} K^{-1} at 60°. Thus $k_f = 5.0 \times 10^2$ s^{-1} at 25° and 4.3×10^3 s^{-1} at 60°.



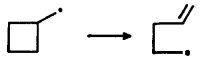
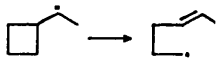
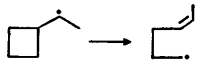
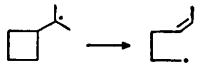
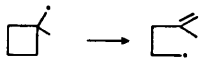
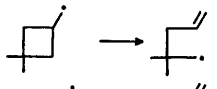
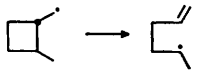
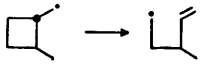
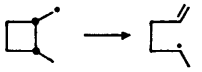
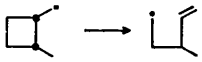
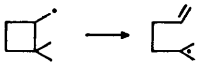
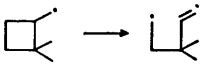
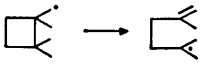
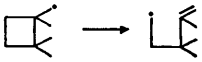
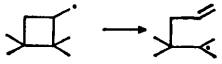
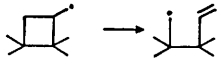
The *A* factor here seems somewhat low for a ring-opening reaction,[22] although it agrees reasonably well with that reported [13a] for ring opening of cyclopropyl-

carbinyl radical: log $A = 12.18$ (after application of the appropriate statistical factor). If the second set of data for k_H is employed we obtain: log $k_f = 12.85 - 13.9/2.3RT$; $\Delta S^{\ddagger} = -2.0$ cal mol^{-1} K^{-1} at 60°. Thus $k_f = 4.5 \times 10^2$ s^{-1} at 25° and 5.3×10^3 s^{-1} at 60°. Whichever is the more correct, it is clear that ring opening of cyclobutylcarbinyl radical, like β-fission of acyclic radicals,[22,27] involves a ' tight ' transition state, and a net loss of entropy associated, presumably, with loss of rotational freedom of the exocyclic methylene groups.

The activation energy, *ca.* 12.5—13.5 kcal mol^{-1}, is unexpectedly high for an exothermic reaction, particularly when compared with the value (*ca.* 6 kcal mol^{-1}) [13a] for cyclopropylcarbinyl radical. Perhaps there are special factors associated with the orbital structure of the latter which facilitate the reaction. Application of the group additivity method [22] to our data suggests that the reverse reaction, *exo*-ring closure of pent-4-enyl radical, should have log A *ca.* 10, E *ca.* 17 kcal mol^{-1}, and k_c *ca.* 10^{-1} s^{-1} at 60°. It is not surprising, therefore, that attempts [16] to detect this type of process have been unsuccessful.

TABLE 1

Kinetic data for ring opening of substituted cyclobutyl carbinyl radicals [a]

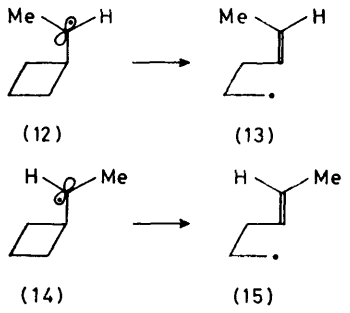
	Reaction	$10^3 k_f/k_H(60°)$ [b]/ mol l^{-1}	$\Delta\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta\Delta S^{\ddagger}$/ cal mol^{-1} K^{-1}	k_{rel}
(A)		2.35 ± 0.1	9.1 ± 0.2	15.4 ± 0.6	1.0
(B1)		1.65 ± 0.1	9.2 ± 0.2	14.9 ± 0.5	0.7
(B2)		0.55 ± 0.1	9.9 ± 0.2	14.8 ± 0.5	0.23
(C)		1.3 ± 0.5			0.75
(D)		1.25 ± 0.05	9.9 ± 0.2	16.4 ± 0.4	0.53
(E)		1.35 ± 0.05	10.5 ± 0.2	18.5 ± 0.5	0.57
(F1)		15.5 ± 0.2	8.5 ± 0.1	17.2 ± 0.2	6.6
(F2)		1.9 ± 0.1	9.6 ± 0.1	16.4 ± 0.3	0.8
(G1)		92.6 ± 0.9	7.6 ± 0.1	18.1 ± 0.2	39.4
(G2)		2 ± 1	9.9 ± 0.9	16.8 ± 0.3	0.8
(H1)		700 ± 20	6.3 ± 0.2	18.2 ± 0.4	300
(H2)		<4			1.5
(I1)		900 ± 20	6.2 ± 0.2	18.4 ± 0.4	380
(I2)		<1			0.4
(J1)		310 ± 10	7.0 ± 0.2	18.8 ± 0.4	132
(J2)		<1			0.4

[a] Uncertainties are expressed as the standard deviation from mean. [b] Values of $k_f/k_H(60°)$ calculated on the basis of the activation parameters shown.

β-Fission of Alkyl-substituted Cyclobutylcarbinyl Radicals.—Fission of the cyclobutylcarbinyl system is

somewhat similar to hexenyl cyclisation [4] in that substitution at the radical centre [C(α)] has little effect on the magnitude of the rate constant. Comparison of the data for reactions (A)—(C) reveals that the order of reactivity is primary > secondary > tertiary but the spread is less than two-fold. Three possible explanations for these observations may be considered: (i) that there is very little delocalisation of the free spin onto the new radical centre at the transition state; (ii) that the differences in thermodynamic stability between primary, secondary, and tertiary radicals are less than is usually accepted; [22,28] and (iii) that the polar influence of substituents compensates for their effects on radical stability. We shall discuss these below in the light of further evidence.

Ring-opening of the α-methylcyclobutylcarbinyl radical [equation (B)] leads to two olefins with the *trans*-isomer predominating (*trans* : *cis* = 3.1). The major factor influencing the isomer distribution is probably the degree of steric crowding in the transition state. If the stereoelectronic requirements for β-fission are to be met then the conformer (12) required for formation of the *cis*-radical (13) must involve an eclipsed non-bonded interaction between the methyl substituent and a ring methylene group which will raise its energy relative to that of the conformer (14) leading to the *trans*-radical (15).



(12) (13)

(14) (15)

Olefinic products are formed in the preparation of the Grignard reagent from 1-chloro-1-cyclobutylethane [29] and it has been suggested that a homolytic ring opening is involved. However, the preferential formation of *cis*-olefins argues against the intermediacy of *free* α-methylcyclobutylcarbinyl radicals in this reaction.

In view of the fact that alkyl substituents at the olefinic seat of reaction strongly retard the rate of cyclisation in the hexenyl system [4] we expected that the cyclobutylcarbinyl radical bearing a methyl group in the equivalent position might undergo rapid ring opening. This is not so. Although β-fission of 1-methylcyclobutylcarbinyl radical [equation (D)] is *ca.* 2 kcal mol^{-1} more exothermic than that of the parent radical [22] it proceeds more slowly. In the case of hexenyl cyclisation the rate-retarding effect of substituents was attributed [4] mainly to the increase in steric compression (*B* strain) engendered at the olefinic carbon on change towards sp^3 hybridisation. We conclude that for cyclobutylcarbinyl fission the transition state is very reactant-like in that the β-carbon has undergone little rehybridisation. Also the β-substituent may slightly impede reaction (D) by sterically hindering the attainment of the disposition of the α-carbon required for efficient orbital overlap.

Cyclobutylcarbinyl radicals bearing substituents at the γ-position [C(2)] undergo ring opening more rapidly than the parent to afford preferentially the more-stable possible product radical [reactions (E)—(J)]. The kinetic parameters show that changes in $\Delta S^{\ddagger}$ are relatively unimportant and that the rate increases are due mainly to favourable changes in the enthalpy term.

The large differences between the effects of substitution at the α- and the γ-position are not readily rationalised, for if the free spin is delocalised over these two positions in the transition state we should, at first sight, expect substituents at one to show effects of similar magnitude but opposite direction to those at the other. One possible explanation stems from Ruchardt's suggestion [28] that alkyl stabilisation of an adjacent radical centre by hyperconjugation is less important than the steric effects of substituents on the changes in compressional energy as a radical centre develops. In ring-opening of the cyclobutylcarbinyl system there is little change in hybridisation or configuration of C(α) during the course of the reaction but C(γ) is transformed from sp^3 to sp^2 hybridisation and the resulting change in configuration relieves both *B* strain and eclipsed interactions with vicinal bonds at C(3). Consequently it is reasonable that substituents at the γ-position should have more pronounced effects than those at the α-position.

Another illustration of the importance of steric effects is provided by the fact that the rate of ring-opening of *cis*-2-methylcyclobutylcarbinyl radical [reaction (G1)], in which there must be strong non-bonded interactions between the vicinal groups, is considerably greater than that of its *trans*-isomer. The rate of the reaction, however, is more sensitive to substitution at C(2) than at C(1). Thus, introduction of a second methyl group at C(2) causes a profound increase in the value of the rate constant [compare reactions (H1) and (G1)], whereas further substitution at C(1) results in only a modest increase [compare reactions (I1) and (H1)]. We conclude that in formation of the transition state the γ-carbon undergoes a more pronounced change in hybridisation than does the β-carbon.

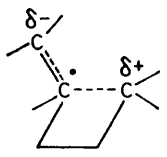
Another additional factor of possible kinetic significance stems from the observation that the 1-methylhex-5-enyl radical and related species preferentially afford *cis*-disubstituted cyclopentane derivatives on cyclisation.[5] This unexpected behaviour is thought to reflect an attractive secondary orbital interaction between the olefinic system and the delocalised radical which stabilises the transition state leading to the *cis*-product. If a similar phenomenon applies to ring-opening of cyclobutylcarbinyl radicals it will enhance the rates of reaction of species containing *cis*-γ-substituents.

The introduction of *gem*-dimethyl groups at the δ-position [C(3)] causes a relatively small decrease in the rate of ring opening of cyclobutylcarbinyl radicals [compare reactions (E) and (J) with (A) and (H)]. This

may be ascribed to the operation of the Thorpe–Ingold or *gem*-dialkyl effect.[30] Such effects powerfully accelerate the rates of cyclisation of appropriately substituted hexenyl [19] and butenyl [31] systems. The fact that they are relatively unimportant here supports the view that the transition state for cyclobutylcarbinyl fission is reactant-like.

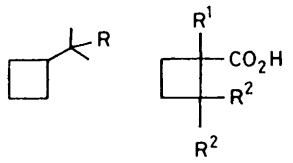
Finally, we consider the question of whether the transition state might be charge-polarised. If the interaction of the semi-occupied orbital with the filled σ-orbital is more effective than with the vacant σ*-orbital then the transition state will have partial dipolar character (16), and its stability will be influenced by the electronic nature of substituents. It has been suggested [20] that the transition states for hexenyl cyclisation and for β-fission of cyclopropylcarbinyl radicals are polarised in that direction which places a fractional positive charge on the α-carbon. This hypothesis accounts for the effects of substituents on the rate of the former reaction and for the remarkable opening of the *trans*-2-methylcyclopropylcarbinyl radical to afford the less-stable product radical.[16] However, in the case of cyclobutylcarbinyl fission the development of charge in the transition state would demand that substituents at the α- and γ-positions should have effects on the reaction rate of similar magnitude but opposite direction. Our kinetic data clearly show that this is not so.

Mechanistic Conclusions.—In summary, the experimental results show that ring opening of cyclobutylcarbinyl radicals is irreversible under the experimental conditions used here. The reaction is under stereoelectronic control and proceeds only when efficient overlap can be attained between the semi-occupied orbital and a βγ-bond. Methyl substitution at the α-, β-, or δ-positions has relatively little effect on the reaction rate. Substituents at the γ-position profoundly enhance the rate of fission of the adjacent βγ-bond. These results are consistent with the hypothesis that the transition state is reactant-like and has a similar disposition of centres to that (1) for homolytic addition. There is no freedom of rotation about the exocyclic 1,α-bond and the transition state is unsymmetrical in that it involves little formation of the new π bond, but some weakening of the βγ-bond and partial rehybridisation of the γ-carbon.



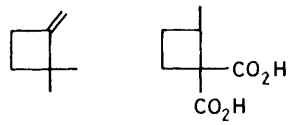
(16)

Preparation of Radical Precursors and Reference Compounds.—The preparation of compounds required as radical precursors or for reference usually followed established methods, but in some cases new or improved techniques were developed which deserve special comment. For example, the methods previously employed [14,29,32] for the conversion of substituted cyclobutylcarbinols into chlorides often give substantial amounts of by-products, whilst thionyl chloride in butane, a reagent which works well with cyclopropylcarbinols,[26] afforded only organic sulphites. Eventually, treatment of toluene-*p*-sulphonates, prepared from the appropriate primary or secondary cyclobutylmethanols, with lithium chloride in hexamethylphosphoric triamide was found to give the required chlorides, substantially free from impurity, and in excellent yield. *NN*-Dimethylformamide was a less satisfactory solvent. Unfortunately the method did not proceed specifically when applied to the tertiary alcohol (17). Here, the best



(17) R = OH
(18) R = Cl

(19) $R^1 = R^2 = H$
(20) R^1 = Me. R^2 = H
(21) R^1 = H. R^2 = Me
(22) $R^1 = R^2$ = Me



(23) (24)

reagent was hydrogen chloride in cold pentane, but it afforded the chloride (18) contaminated by 1-chloro-2,2-dimethylcyclopentane, which was partially removed by g.l.c.

Methylation of the dianion generated by treatment of cyclobutanecarboxylic acid (19) with lithium di-isopropylamide [33] proceeded in very good yield to provide a shorter and more efficient route to the acid (20) than was previously available.[34,35] This procedure was also applied successfully to methylation of the acid (21). An attempt to prepare the acid (22) more directly by treatment of the olefin (23) with nickel carbonyl [35] gave a poor yield.

The use of sodium hydride in *NN*-dimethylformamide for the preparation of the di-ester (24) *via* a malonic ester synthesis, gave a cleaner product than the conventional procedure,[36] and, contrary to a recent report,[14] did not initiate elimination.

The *endo*-chloride (3) was formed stereospecifically when the toluene-*p*-sulphonate of *exo*-bicyclo[3.2.0]-heptan-2-ol was treated with lithium chloride in hexamethylphosphoric triamide. Although some elimination occurred there was no evidence of the rearrangements which sometimes accompany syntheses of 2-halogenobicyclo[3.2.0]heptanes.[15,37]

EXPERIMENTAL

General experimental details have been given previously.[8] The following columns were used for g.l.c.: (A) 6.3 m × 3.2 mm, 0.75% FFAP on Varaport 30 stainless steel column; (B) 3 m × 7 mm, 14% Carbowax 20M–TPA on Chromasorb A glass column; (C) 6 m × 8 mm, 30% QF 1–NPGS (2 : 1) on Chromasorb A glass column; (D) 2 m × 7 mm, 20% QF 1 on Varaport 30 glass column; (E) 1.4 m × 7 mm, 17% FFAP on Varaport 30 glass column; (F) 6 m × 3.2 mm, 20% propylene carbonate on Varaport 30 glass column; (G) 70 m × 0.5 mm, squalane glass SCOT column; (H) 4.6 m × 2.1 mm, 5% Apiezon M on Varaport 30 glass column; (I) 2 m × 3.2 mm, 40% silver nitrate–benzyl cyanide on Chromasorb W stainless steel column; (J) 3 m × 3.2 mm, 20% dimethylsulpholan on Chromasorb W glass column. Nitrogen was used as carrier gas with flow rate of 2 ml min^{-1} for column (G), 20 ml min^{-1} for other analytical columns, and 60 ml min^{-1} for preparative columns. Unless otherwise stated the purity (>99%) of all chloro-compounds and reference materials used in this work was established by analytical g.l.c.

Chloromethylcyclobutane.—A solution of cyclobutylmethanol [38] (2.9 g) and toluene-*p*-sulphonyl chloride (12.6 g) in pyridine (55 ml) was kept at 0° for 24 h, then treated with water (5 ml) in pyridine (5 ml) to destroy the excess of reagent, and poured into ice–water. The mixture was extracted with ether, and the ether layer was washed successively with cold 2% hydrochloric acid, 10% sodium carbonate solution, and water. After being dried the solution was evaporated *in vacuo* to afford the toluene-*p*-sulphonate as a pale yellow oil (7.5 g, 92%), a sample (2.9 g) of which was mixed with lithium chloride (1.8 g) in hexamethylphosphoric triamide (25 ml) and stirred at ambient temperature for 15 h. Water and light petroleum were then added, and the organic layer was separated, washed with water, dried, and fractionally distilled to give 1-chloromethylcyclobutane [29] (1.2 g, 97%), b.p. 109—111°, n_D^{21} 1.448. The n.m.r. spectrum [29] and g.l.c. analysis (column A; 50°) showed the chloride to be free from impurity. A similar experiment in which *NN*-dimethylformamide was employed as solvent gave 50% of the chloride after a longer reaction time (84 h).

1-*Chloro*-1-*cyclobutylethane*.—1-Cyclobutylethanol [29] (6.5 g) was converted by treatment of its toluene-*p*-sulphonate with lithium chloride in hexamethylphosphoric triamide as described above into 1-chloro-1-cyclobutylethane [29,39] (5.2 g, 76%), b.p. 126—128°, n_D^{23} 1.444, which was shown by g.l.c. (column A; 80°) to contain a trace (<3%) of impurity. The sample used for kinetic work was further purified by preparative g.l.c. (column B; 110°).

2-*Chloro*-2-*cyclobutylpropane*.—Dry hydrogen chloride was slowly introduced into a solution of 2-cyclobutylpropan-2-ol [40] (0.52 g; prepared by a Grignard reaction of methyl cyclobutanecarboxylate) in pentane (2 ml) at 0° until g.l.c. (column A; 60°) indicated 95% conversion of starting material into product. The excess of hydrogen chloride was then removed by gentle aspiration, and the solution was dried over potassium carbonate. Preparative g.l.c. (column B; 90°) afforded a mixture of 2-chloro-2-cyclobutylpropane (92%), δ 1.25 (6 H, s, 2 × CH_3) and 1.7—2.7 (7 H, complex, ring H), and 1-chloro-2,2-dimethylcyclopentane (8%), δ 1.05 (6 H, s, 2 × CH_3), 1.4—2.4 (6 H, complex, ring H), and 3.8 (1 H, t, *J* 6 Hz, CHCl). The identity of the contaminant was confirmed by the fact that reduction of the mixture of chlorides with tributylstannane afforded, *inter alia*, 8% of 1,1-dimethylcyclopentane. When 2-cyclobutylpropan-2-ol (0.50 g) was treated with phosphorus pentachloride (1.0 g; freshly sublimed) in methylene chloride (10 ml) at −20° for 2 h the product comprised a mixture of the same two chlorides in the ratio 1.5 : 1.

1-*Methylcyclobutanecarboxylic Acid*.—Cyclobutanecarboxylic acid (4.0 g) was added with stirring to lithium di-isopropylamide [prepared from butyl-lithium in pentane (96 ml, 1M) and di-isopropylamine (9.7 g) in tetrahydrofuran (30 ml) at −10°] at such a rate that the temperature could be maintained at 0°. After the mixture had been stirred at ambient temperature for 0.5 h, methyl iodide (6.8 g) was added dropwise, and stirring was continued for a further 3 h. Hydrochloric acid (20%) was then added, the mixture was extracted with ether, and the ether layer was washed, dried, and evaporated *in vacuo*. Distillation of the residue afforded 1-methylcyclobutanecarboxylic acid [34] (4.0 g, 88%), b.p. 101—105° at 17 mmHg, which was shown by g.l.c. (column A; 100°) of its ethyl ester to contain <5% of starting material. A product of >98% purity could be obtained by further alkylation of the crude acid.

1-*Chloromethyl*-1-*methylcyclobutane*.—When 1-methylcyclobutylmethanol (2.3 g; prepared by reduction of the foregoing acid with lithium aluminium hydride [32]) was treated in the usual way (see above) with lithium chloride in hexamethylphosphoric triamide and the product (2.0 g, 93%) was purified by preparative g.l.c. (column C; 130°) there was obtained 1-chloromethyl-1-methylcyclobutane, b.p. 125—130° (lit.,[32] 122—130°), n_D^{24} 1.445 (Found: C, 60.8; H, 9.3. Calc. for $C_6H_{11}Cl$: C, 60.8; H, 9.4%).

cis-1-*Chloromethyl*-2-*methylcyclobutane*.—Reduction of *cis*-2-methylcyclobutanecarboxylic acid [41] with lithium aluminium hydride in ether afforded *cis*-2-methylcyclobutylethanol. Treatment of its toluene-*p*-sulphonate with lithium chloride in the usual way gave the required chloride (87%) contaminated with a trace (<1%) of the *trans*-isomer. Preparative g.l.c. (column B; 90°) afforded a pure sample of *cis*-1-chloromethyl-2-methylcyclobutane,[15] n_D^{20} 1.443 (Found: C, 60.4; H, 9.3%).

trans-1-*Chloromethyl*-2-*methylcyclobutane*.—Diethyl malonate (96 g) was added dropwise to a stirred suspension of sodium hydride (29 g; 50% dispersion in oil) in *NN*-dimethylformamide (140 ml) at ambient temperature. After 30 min the black suspension was added slowly with stirring under nitrogen to 1,3-dibromobutane (130 g), and the mixture was then stirred at ambient temperature for 3 h. A further quantity of sodium hydride (29 g; 50% dispersion) was then added in small portions during 1 h. After being stirred for 15 h the mixture was poured into water and extracted with ether to afford diethyl 2-methylcyclobutane-1,1-dicarboxylate [36] (50.1 g, 39%), b.p. 82—85° at 0.3 mmHg (lit.,[36] 70—72.5° at 1 mmHg), which was shown by g.l.c. (column A; 160°) to contain <2% of impurity.

This diester was hydrolysed, decarboxylated, and reduced with lithium aluminium hydride [36] to afford a mixture of the *cis*- and *trans*-isomers of 2-methylcyclobutylmethanol which was converted into toluene-*p*-sulphonates and treated with lithium chloride as described above. The product comprised a mixture of *cis*- and *trans*-chlorides (*cis* : *trans* 1 : 3), preparative g.l.c. (column B; 85°) of which afforded a pure (>99%) sample of *trans*-1-chloromethyl-2-methylcyclobutane,[14] n_D^{19} 1.443 (Found: C, 61.3; H, 9.8%).

2-*Chloromethyl*-1,1-*dimethylcyclobutane*.—The toluene-*p*-

sulphonate of 2,2-dimethylcyclobutylmethanol [42] was treated with lithium chloride as described above. Preparative g.l.c. (column B; 100°) of the product (94%) afforded a pure sample of 2-*chloromethyl*-1,1-*dimethylcyclobutane*, n_D^{24} 1.446 (Found: C, 63.9; H, 9.8. $C_7H_{13}Cl$ requires C, 63.4; H, 9.9%); δ 1.05 (3 H, s, CH_3), 1.15 (3 H, s, CH_3), 1.3—2.6 (5 H, complex, ring H), and 3.4 (2 H, m, CH_2Cl).

Ethyl 1,2,2-*Trimethylcyclobutanecarboxylate*.—2,2-Dimethylcyclobutanecarboxylic acid [42] (2.8 g) was converted into its dianion and methylated as described above to give impure 1,2,2-trimethylcyclobutanecarboxylic acid (2.7 g, 88%) a sample of which was converted to the ethyl ester by treatment with diazoethane. The product was shown by g.l.c. (column A; 140°) to contain 91% of the required ester. Preparative g.l.c. (column D; 125°) afforded pure *ethyl* 1,2,2-*trimethylcyclobutanecarboxylate*, n_D^{18} 1.4331 (Found: C, 70.9; H, 10.7. $C_{10}H_{18}O_2$ requires C, 70.6; H, 10.7%), $\nu_{max.}$ 1 740 cm^{-1}, δ 1.05 (6 H, s, 2 × CH_3), 1.25 (3 H, t, *J* 4 Hz, OCH_2CH_3), 1.3 (3 H, s, CH_3), 1.02—2.7 (4 H. complex, CH_2CH_2), and 4.15 (2 H, q, *J* 4 Hz, OCH_2).

1,2,2-*Trimethylcyclobutylmethanol*.—The foregoing crude acid (2.4 g), when reduced with lithium aluminium hydride in ether gave impure alcohol (1.9 g, 88%), preparative g.l.c. (column D; 100°) of which afforded 1,2,2-*trimethylcyclobutylmethanol*, m.p. 113—114° (Found: C, 75.7; H, 12.6. $C_8H_{16}O$ requires C, 74.9; H, 13.0%), δ 1.05 (9 H, 3 partially resolved s, 3 × CH_3), 1.6 (4 H, complex, CH_2CH_2), and 3.55 (2 H, m, appears as the AB portion of an ABX pattern with J_{AB} 6 Hz, CH_2O).

1-*Chloromethyl*-1,2,2-*trimethylcyclobutane*.—Treatment of the toluene-*p*-sulphonate of the foregoing alcohol (2.9 g) with lithium chloride as described above gave a mixture (2.9 g, 85%) of the required chloride (90%) and 1-chloromethyl-2,2-dimethylcyclobutane (10%). The contaminant was removed by preparative g.l.c. (column B, 120°) to afford 1-*chloromethyl*-1,2,2-*trimethylcyclobutane* as a waxy solid, m.p. 40° (Found: C, 65.9; H, 10.1. $C_8H_{15}Cl$ requires C, 65.9; H, 10.3%), δ 1.4 (6 H, s, 2 × CH_3), 1.5 (3 H, s, CH_3), 2.0 (4 H, m, CH_2CH_2), 3.85 (2 H, m, appears as the AB portion of an ABX pattern with J_{AB} 5 Hz, CH_2Cl).

3-*Chloromethyl*-1,1-*dimethylcyclobutane*.—A mixture of t-butyl 2-dimethylamino-3,3-dimethylcyclobutanecarboxylate [43] (34 g) and methyl iodide (27 g) was heated at 80° for 4 h. The excess of methyl iodide was then evaporated *in vacuo* and potassium hydroxide (22 g) in water (60 ml) was added. After being heated at 80° for 16 h the mixture was extracted with ether to afford a crude ester (8.3 g, 30%), which was hydrogenated in ether at 3 atmospheres over Adams catalyst. Preparative g.l.c. (column E; 100°) of the product afforded *t-butyl* 3,3-*dimethylcyclobutanecarboxylate*, n_D^{20} 1.562 (Found: C, 71.5; H, 11.0. $C_{11}H_{20}O_2$ requires C, 71.7; H, 10.9%), δ 0.95 (3 H, s, CH_3), 1.0 (3 H, s, CH_3), 1.3 (9 H, s, Bu^t), and 1.7—2.1 (5 H, complex, ring H).

The aqueous layer remaining after extraction of the t-butyl ester was acidified and extracted with ether to give, after crystallization from hexane, 3,3-dimethylcyclobut-1-enecarboxylic acid [44] (5 g, 27%), m.p. 70—72°. Hydrogenation of this acid, and reduction of the product with lithium aluminium hydride, gave 3,3-dimethylcyclobutylmethanol,[36] which was treated with lithium chloride as described above to afford 1-chloromethyl-3,3-dimethylcyclobutane, b.p. 60° (block) at 100 mmHg, n_D^{21} 1.438 (Found: C, 63.8; H, 9.8. $C_7H_{13}Cl$ requires C, 63.4; H, 9.8%), δ 1.05 (3 H, s, CH_3), 1.15 (3 H, s, CH_3), 1.3—3.2 (5 H, complex, ring H), and 3.5 (2 H, d, CH_2Cl).

3-*Chloromethyl*-1,1,2,2-*tetramethylcyclobutane*.—Treatment of the toluene-*p*-sulphonate of 2,2,3,3-tetramethylcyclobutylmethanol (1.0 g) [42] with lithium chloride in hexamethylphosphoric triamide (see above) afforded a liquid (1.1 g, 97%), preparative g.l.c. (column B; 120°) of which gave 3-*chloromethyl*-1,1,2,2-*tetramethylcyclobutane*, n_D^{22} 1.4351 (Found: C, 67.3; H, 10.6. $C_9H_{17}Cl$ requires C, 67.3; H, 10.7%), δ 0.9 (3 H, s, CH_3), 1.0 (6 H, s, 2 × CH_3), 1.05 (3 H, s, CH_3), 1.3—1.9 (2 H, m, ring H), 2.0—2.7 (1 H, m, CH), and 3.3—3.6 (2 H, m, CH_2Cl).

endo-2-*Chlorobicyclo*[3.2.0]*heptane*.—Solvolysis of the toluene-*p*-sulphonate of *syn*-bicyclo[2.2.1]hept-2-en-7-ol [45] in aqueous sodium hydrogencarbonate gave *exo*-bicyclo-[3.2.0]hept-3-en-2-ol, b.p. 100—104° at 200 mmHg, *m/e* 110 (M^+), δ 0.9—3.0 (7 H, complex), 3.2—3.4 (1 H, m, CH), 4.5 (1 H, m, CHOH), and 5.9—6.3 (2 H, m, CH=CH). This alcohol was hydrogenated over Adam's catalyst, and the product converted into its toluene-*p*-sulphonate, treatment of which with lithium chloride in the usual way afforded a mixture, separated by preparative g.l.c. (column B; 120°), of bicyclohept-2-ene (35%) and the required chloride,[15,37] b.p. 49—50° (block) at 20 mmHg.

5-*Chloro*-3-*methylpent*-1-*ene*.—The toluene-*p*-sulphonate prepared from 3-methylpent-4-en-1-ol (1.8 g) was stirred with lithium chloride (1.5 g) in *NN*-dimethylformamide (45 ml) at ambient temperature for 48 h and the mixture was then poured into water. Extraction with pentane gave the required chloride (2.0 g, 94%), b.p. 124—126° (Found: C, 61.1; H, 9.4. $C_6H_{11}Cl$ requires C, 60.8; H, 9.4%).

3-(2-*Chloroethyl*)*cyclopentene*.—Treatment of 3-(2-hydroxyethyl)cyclopentene [46] with lithium chloride in *NN*-dimethylformamide as described above gave, after preparative g.l.c. (column B; 120°) of the crude product (51%), the required *chloro-compound*, b.p. 40° (block) at 50 mmHg (Found: C, 64.6; H, 8.5. $C_7H_{11}Cl$ requires C, 64.4; H, 8.5%), δ 1.4—3.1 (7 H, complex), 3.6 (2 H, t, *J* 7 Hz, CH_2Cl), and 5.7 (2 H, m, CH=CH).

Ethylcyclobutane.—Wolff–Kishner reduction of acetylcyclobutane gave ethylcyclobutane,[47] n_D^{20} 1.402, δ 0.75 (3 H, t, *J* 7 Hz, CH_3) and 1.0—2.2 (9 H, complex).

Isopropylcyclobutane.—Acetylcyclobutane was converted into isopropenylcyclobutane by a Wittig reaction in dimethyl sulphoxide,[42] and the crude product was hydrogenated over Adam's catalyst in ether to afford, after preparative g.l.c. (column B; 40°), a pure sample of isopropylcyclobutane,[48] n_D^{20} 1.4078, δ 0.8 (6 H, d, *J* 6 Hz, 2 × CH_3) and 1.2—2.2 (8 H, complex).

1,1-*Dimethylcyclobutane*.— Cyclobutane-1,1-dicarboxylic acid on reduction with lithium aluminium hydride gave 1,1-bis(hydroxymethyl)cyclobutane, which was converted by the usual procedure into its bistoluene-*p*-sulphonate. The latter (8.9 g) was stirred with lithium aluminium hydride (3.2 g) in diglyme (30 ml) at 50° for 16 h, after which time the temperature was raised to 140°. The product (1.2 g, 67%), which distilled directly from the mixture, contained <5% impurity (column H; 40°). Preparative g.l.c. (column B; 40°) gave a pure sample of 1,1-dimethylcyclobutane, n_D^{20} 1.394, δ 1.1 (6 H, s, 2 × CH_3) and 1.75 (6 H, s, ring H).

1,1,3-*Trimethylcyclobutane*, cis- *and* trans-1,2-*Dimethylcyclobutane, and* 1,1,2-*Trimethylcyclobutane*.—The foregoing three step procedure when applied to the appropriate acids gave 1,1,3-*trimethylcyclobutane* (from 3,3-dimethylcyclobutanecarboxylic acid), n_D^{20} 1.402 (Found: C, 86.0; H, 14.3. C_7H_{14} requires C, 85.6; H, 14.4%), δ 0.95—1.15 (9 H, a

doublet and two singlets incompletely resolved, 3 × CH_3), and 1.0—2.7 (5 H, complex, ring H); *trans*-1,2-dimethylcyclobutane [49] (from *trans*-cyclobutane-1,2-dicarboxylic acid), n_D^{20} 1.389; *cis*-1,2-dimethylcyclobutane [50] (from *cis*-cyclobutane-1,2-dicarboxylic anhydride), n_D^{20} 1.403, δ 0.95 (6 H, d, *J* 6 Hz, CH_3), 1.1—2.7 (6 H, complex, ring H) ; and 1,1,2-trimethylcyclobutane [51] (from 2-methylcyclobutane-1,1-dicarboxylic acid, also by hydrogenation of 2,2-dimethylmethylenecyclobutane), n_D^{20} 1.406 (Found: C, 85.9; H, 14.4. C_7H_{14} requires, C, 85.6; H, 14.4%), δ 0.7—1.0 (9 H, a doublet and two singlets partially resolved, 3 × CH_3) and 1.4—2.4 (5 H, complex, ring H).

1,1,2,2-*Tetramethylcyclobutane*.—Preparative g.l.c. (column B; 60°) of the crude product from Wolff–Kishner reduction of 2,2,3,3-tetramethylcyclobutanone [43] gave 1,1,2,2-*tetramethylcyclobutane* as a waxy solid, m.p. *ca.* 40° (Found: C, 85.0; H, 14.4. C_8H_{16} requires C, 85.6; H, 14.4%), δ 0.95 (12 H, s, 4 × CH_3) and 1.6 (4 H, s, CH_2CH_2).

1,1,2,2,3-*Pentamethylcyclobutane*.—Hydrogenation of 2,2,3,3-tetramethylmethylenecyclobutane [42] in ether over Adam's catalyst, and purification of the crude product by preparative g.l.c. (column B; 60°) gave 1,1,2,2,3-*pentamethylcyclobutane* (Found: C, 86.0; H, 14.2. C_9H_{18} requires C, 85.6; H, 14.4%).

Bicyclo[3.2.0]*heptane*.—Hydrogenation of bicyclo[3.2.0]-hept-2-ene in ether over Adam's catalyst gave bicyclo-[3.2.0]heptane,[43] n_D^{19} 1.4532.

3-*Ethylcyclopentene and Cycloheptene*.—These were prepared by previously described methods.[52]

Acyclic Olefins.—*cis*-Hex-2-ene, 2-methylhex-2-ene, and 2-methylpent-1-ene, when prepared by the Wittig procedure, and purified by preparative g.l.c. (column B; 30°) each had physical constants in agreement with literature values.[53]

3-Methylpent-1-ene and 5-methylhex-1-ene were each prepared by pyrolysis of the appropriate acetate (prepared respectively from 3-methylpentan-1-ol and 5-methylhexan-1-ol), by slow distillation through a column packed with silica beads at 500°, and were purified by preparative g.l.c. (column B; 30°).

3,3-*Dimethylpent*-1-*ene* was similarly prepared by pyrolysis of 1,2,3-trimethylbutyl acetate, b.p. 90—100° at 20 mmHg, n_D^{18} 1.4192 (Found: C, 68.6; H, 11.2. $C_9H_{18}O_2$ requires C, 68.3; H, 11.5%).

4,4-Dimethylpent-1-ene, 2,2,3-trimethylpent-1-ene, and 4,5,5-trimethylhex-1-ene were each prepared by methods previously described.[42,54]

2,5-*Dimethylhex*-1-*ene*.—3-Chloro-2-methylpropene (5.4 g) was added to the Grignard reagent from 1-bromo-2-methylpropane (9 g) and magnesium turnings (3.7 g) in tetrahydrofuran (20 ml). After addition of lithium tetrachlorocuprate in tetrahydrofuran [55] (2 ml, 0.1M) to the cooled (0°) solution it was stirred for 3 h at 0° then poured onto ice. The usual work-up gave 2,5-dimethylhex-1-ene [53] (3 g, 45%), b.p. 112—115°, n_D^{20} 1.4085, which was purified by preparative g.l.c. (column B; 90°).

The Reduction of Chloro-compounds with Tributylstannane.—Tri-n-butylstannane, the chloride (1.2—1.5 equiv.), and an internal standard were each accurately weighed into a volumetric flask which was then filled with solvent (decalin unless otherwise stated) to give the required concentration. This solution was then pipetted into ampoules (1 ml, each containing a trace of azobisisobutyronitrile as radical initiator) which were cooled at −78°, deoxygenated with a stream of nitrogen, and sealed. The ampoules were then immersed in constant temperature baths at the required temperature (±0.2°) for 24 h, at which time they were cooled, opened, and the contents analysed by g.l.c.

TABLE 2

Reduction of chloromethylcyclobutane (7)

Temperature (°C)	$[Bu_3SnH]_0$ [a] / M	Relative yield %(9)	Relative yield %(11)	Total yield (%)	$10^2\ k_t/k_H$ mol l^{-1}
59.9	0.011	49.4	50.6		0.42
59.9	0.054	78.3	21.7	75.5	0.46
59.9	0.073	81.8	18.2	76.2	0.47
60.1	0.010	49.4	50.6	55.4	0.42
60.1	0.012	51.9	48.1	67.7	0.45
60.1	0.052	77.7	22.3	84.3	0.46
60.1	0.062	80.0	20.0	81.1	0.46
70.1	0.054	71.6	28.4	79.7	0.71
70.1	0.073	74.9	25.1	78.1	0.75
90.3	0.054	58.5	41.5	85.3	1.44
90.3	0.073	63.9	36.1	80.3	1.43

[a] Initial concentration of tributylstannane.

Products of the free radical reaction were in each case identified by comparison of their g.l.c. retention times with those of authentic samples on at least two columns of widely different separation characteristics. In general, columns F and G were used for this purpose, though in specific cases, where the desired separation was not obtained, columns H—J were also used.

For quantitative determination of reaction produces, the product mixtures were analysed using that column (of F or G) which afforded the best separation. Mixtures containing accurately known amounts of each of the reaction products in decalin were also analysed to determine the molar response ratios. In no case was this ratio found to deviate more than ±2% from unity. The product ratios could, in general, be determined to be better than ±1%. The errors were magnified in cases where a compound constituted <5% of the total hydrocarbon product. However, the total yield of products could not be determined at better than ±3%.

Control experiments were conducted as follows. (a) Samples of the chlorides in decalin, containing tributyltin chloride, were heated at 60° or at 100° for 48 h. G.l.c. analysis indicated a quantitative recovery of the chloride. No hydrocarbon products were formed from these reactions. (b) A halide (either bromocyclohexane or 2-chlorobutane) was reduced with tributylstannane in the presence of

samples of representative olefins (hex-1-ene, *cis*-hex-2-ene, *trans*-hept-2-ene, pent-2-ene, 2-methylhex-2-ene, and 2-ethylcyclopentene) the reaction conditions approximating those used for the kinetic runs. A portion of the terminal and cyclic olefins was consumed under conditions where a large excess of tributylstannane was used. The recovery of olefin depended on the relative and absolute concentration of tributylstannane and the conditions of analysis. Consequently no precise estimate of the amount of olefin consumed could be made. The olefins were stable in the presence of an excess of the halide.

Acyclic disubstituted and trisubstituted olefins were stable under all conditions used. However, they were found to undergo *cis–trans* isomerisation to form an equilibrium mixture of isomers when an excess of stannane was used. The olefins were configurationally stable in the presence of excess of chloride at stannane concentrations below 0.1M.

Values of the rate constant ratio k_t/k_H were determined by solving the appropriate integrated rate equation [6] by a computer-based iterative procedure. For the reactions conducted under ' normal ' reduction conditions (*i.e.* in the presence of excess chloride) the total yield of hydrocarbon products was normalised to 100% for computational purposes; the final stannane concentration being assumed to be zero (residual halide was detected in the reaction mixtures; however, a precise determination could not be made). The values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ presented in Table 1 were determined by a least-squares treatment of the relative rate constants using a modified ACTENG program.[50]

RESULTS

Each reaction was run at three or more different concentrations giving at least a five-fold variation, and at three or more different temperatures. Data for the reduction of chloromethylcyclobutane are given in Table 2. Full results for other reactions are available.[57] The following compilation contains typical data for each compound at one temperature. The order of listing is: reaction, chlorocompound, temperature, initial stannane concentration, total yield, products (relative yield), and k_t/k_H: (B), 1-chloro-1-cyclobutylethane, 60.2°, 0.024M, 92%, ethylcyclobutane (65.3%), *trans*-hex-2-ene (26.2%), *cis*-hex-2-ene (8.5%), 4.5×10^{-3}; (C), 2-chloro-2-cyclobutylpropane, 60.2°, 0.019M (stannane in ten-fold excess), 100%, isopropylcyclobutane (87.6%), 2-methylhex-2-ene (12.4%), 2.6×10^{-3}; (D) 1-chloromethyl-1-methylcyclobutane, 59.9°, 0.027M, 83%, 1,1-dimethylcyclobutane (77.7%), 2-methylhex-1-ene (22.3%), 2.4×10^{-3}; (E) 3-chloromethyl-1,1-dimethylcyclobutane, 60.2°, 0.046M, 90%, 1,1,3-trimethylcyclobutane (83.2%), 4,4-dimethylpent-1-ene (16.8%), 2.7×10^{-3}; (F) *trans*-1-chloromethyl-2-methylcyclobutane, 60.2°, 0.121M, 82%, *trans*-1,2-dimethylcyclobutane (69.9%), hex-1-ene (26.8%), 3-methylpent-1-ene (3.3%), 1.8×10^{-2}; (G) *cis*-1-chloromethyl-2-methylcyclobutane, 60.6°, 0.196M, 80%, *cis*-1,2-dimethylcyclobutane (45.3%), hex-1-ene (53.6%), 3-methylpent-1-ene (1.1%), 9.7×10^{-2}; (H) 2-chloromethyl-1,1-dimethylcyclobutane, 60.3°, 0.880M, 86%, 1,1,2-trimethylcyclobutane (35.0%), 5-methylhex-1-ene (65.0%), 3,3-dimethylpent-1-ene (trace), 0.71; (I) 1-chloromethyl-1,2,2-trimethylcyclobutane, 60.2°, 0.685M, 87%, 1,1,2,2-tetramethylcyclobutane (25.7%), 2,5-dimethylhex-1-ene (74.3%), 2,3,3-trimethylpent-1-ene (trace), 0.90; (J) 3-chloromethyl-1,1,2,2-tetramethylcyclobutane, 60.2°, 0.612M, 92%, 1,1,2,2,3-pentamethylcyclobutane (44.8%), 4,4,5-trimethylhex-1-ene (55.2%), 0.31 (3,3,4,4-tetramethylpent-1-ene could not be detected); (K) 2-chlorobicyclo[3.2.0]heptene, 80.1°, 0.021M, 77%, bicyclo[3.2.0]heptane (74.3%), 3-ethylcyclopentene (26.6%), 2.5×10^{-2}.

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