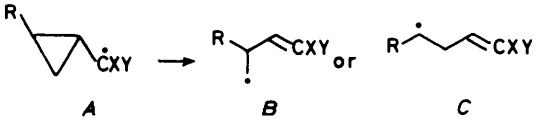
Regioselectivity in the Ring Opening of 2-Alkylcyclopropylmethyl Radicals: the Effect of Electronegative Substituents

Max Ratier and Michel Pereyre
Laboratoire de Chimie des Composés Organiques du Silicium et de l'Etain, associé au CNRS, Université de Bordeaux I, 351 Cours de la Liberation, 33405 Talence, France
Alwyn G. Davies and Roger Sutcliffe
Chemistry Department, University College London, 20 Gordon Street, London WC1:H0AJ

The regioselectivity of the ring-opening of the *trans*-2-alkylcyclopropylmethyl radical *A* to give the primary alkyl radicals *B*, or the secondary alkyl radicals *C*, has been investigated, where the groups R



(R, ĊXY ≡ CF_3, $\dot{C}MeCH_2SnR'_3$; CH_3, ĊHCl; CH_3, ĊHCN; CF_3, ĊHCl; CF_3, ĊHCN; CF_3, ĊHOH; CH_3, $\dot{C}Cl_2$)

and/or CXY carry electronegative substituents. All these reactions gave principally the secondary alkyl radicals *C*, whereas, in the absence of electronegative substituents, ring-opening occurs in favour of the primary alkyl radicals *B*. This regioselectivity is interpreted in terms of the frontier orbital interactions which are involved.

Cyclopropylcarbinyl radicals undergo β-scission to give allylcarbinyl radicals. Our interest has been in the unusual regioselectivity which is observed when the cyclopropyl ring carries an alkyl substituent in the 2-position (Scheme 1).[1-11]

The *cis*-isomers (**1**) give preferentially the secondary alkyl radicals (**3**), but the *trans*-isomers (**2**) give preferentially the thermodynamically less stable primary alkyl radicals (**4**). Ref. 11 lists some 15 examples of the reaction (**2**) ⟶ (**4**). No exception to this rule of regioselectivity appears to be known when R is an alkyl group; only when R is phenyl is the secondary radical (**3**) formed, presumably because of benzylic stabilisation.[3,10]

We have proposed that the regioselectivity (**2**) ⟶ (**4**) can be understood in terms of the frontier orbital interactions which are involved (Figure 1). Electron release by the alkyl group R raises the energies of the σ and σ* orbitals of the C(1)–C(2) bond above those of the C(1)–C(3) bond. If the interaction of the 2*p* SOMO of the ĊXY radical is primarily with the σ* rather than the σ orbital, this can lead to cleavage of the C(1)–C(3) bond. In the *cis*-derivative, any such effect is over-ridden by steric interference between the two *cis* substituents in the conformation which would lead to C(1)–C(3) cleavage.[11]

A similar interpretation has been proposed independently by Mariano.[12]

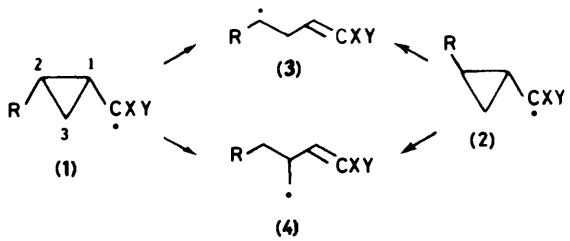
The present paper describes the results of experiments designed to test this hypothesis.

If the substituent R is designed to be electron attracting with respect to the cyclopropyl ring, rather than electron releasing, the order of the energy levels of the σ* (and σ) C(1)–C(2) and C(2)–C(3) bonds should be reversed, leading to cleavage of the C(1)–C(2) rather than the C(1)–C(3) bond (Figure 2).

Similarly, if the SOMO energy of the radical could be reduced, rendering it more 'electrophilic', a point might be reached at which interaction with the σ rather than the σ* C–C bond orbitals becomes dominant, when the C(1)–C(2) bond should cleave if R is electron releasing (Figure 3).

If both the substituent R, and the groups X and Y at the radical centre, were made electronegative, the outcome would be less predictable as the relative importance of the interaction of the SOMO with the σ (HOMO) or σ* (LUMO) orbitals of the ring would depend on the relative magnitudes of the two electronic effects (Figure 4).

Cyclopropyl compounds have been prepared where the



Scheme 1.

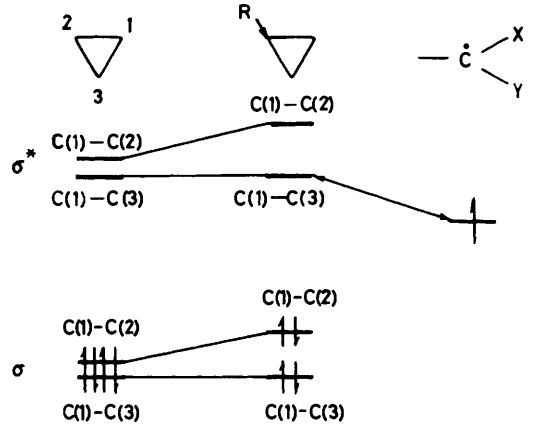


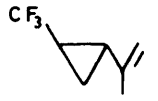
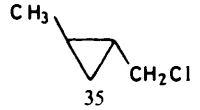
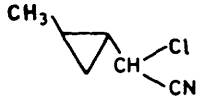
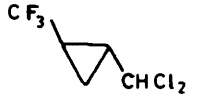
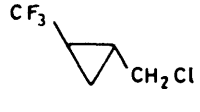
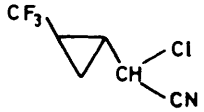
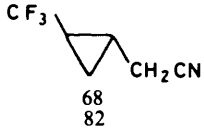
Figure 1. R electron releasing, SOMO–σ*C(1)–C(3) interaction.

substituents in the ring or at the potential radical centre are electronegative. The radicals have been generated, and the regioselectivity of ring-opening determined by analysis of the products or by e.s.r. examination of the radical intermediates, and the results are discussed in terms of the above model.

Results

Product Analysis.—The experiments involving the analysis of the products of ring-opening made use of the homolytic

Table 1. Products of reductive ring-opening of cyclopropylcarbinyl compounds

Reactant	Reagent	T/°C	Products, composition (%)		
	Me_3SnH	+25	$CF_3CH_2CH_2CH{=}CMeCH_2SnMe_3$ 80	$CF_3CHMeCH{=}CMeCH_2SnMe_3$ 20	
			$CF_3CH_2CH_2CH_2CMe{=}CH_2$	$CF_3CHMeCH_2CMe{=}CH_2$	
	(i) Me_3SnH (ii) HBr	+25	80	20	
	(i) Bu_3SnH (ii) HBr	+25	73	27	
		−25	80	20	
	Bu_3SnH	+25	$CH_3CH_2CH_2CH{=}CHCl$ 74	$CH_3CHMeCH{=}CHCl$ 26	
		−25	63	37	
		−80	40	25	35
	Bu_3SnH	−20	$CH_3CH_2CH_2CH{=}CHCN$[a] 100	$CH_3CHMeCH{=}CHCN$ 0	
	Bu_3SnH	+25	$CF_3CH_2CH_2CH{=}CHCl$ 64[b]	$CF_3CHMeCH{=}CHCl$ 14[c]	
		−25	34[b]	10[c]	56
	Bu_3SnH	+25	$CF_3CH_2CH_2CH{=}CHCN$ 32[e]	0	 68
		−25	18[f]	0	82
		+25[d]	79[g]	0	21

[a] 60% *cis*, 40% *trans*. [b] 73% *trans*, 27% *cis*. [c] 78% *trans*, 22% *cis*. [d] In heptane solution, [Bu_3SnH] 0.072M, [chloronitrile] 0.178M. [e] 58% *cis*, 42% *trans*. [f] 57% *cis*, 43% *trans*. [g] 36% *cis*, 64% *trans*.

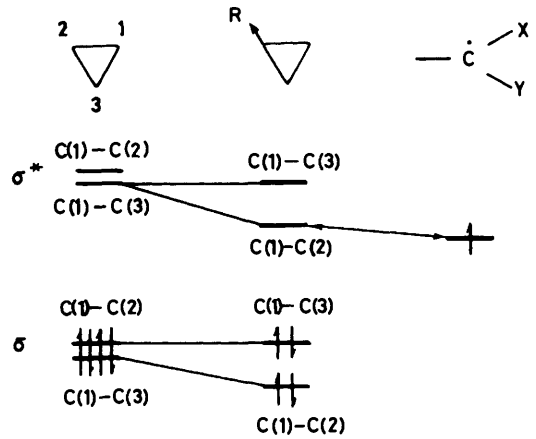


Figure 2. R electron attracting, SOMO–σ*C(1)–C(2) interaction

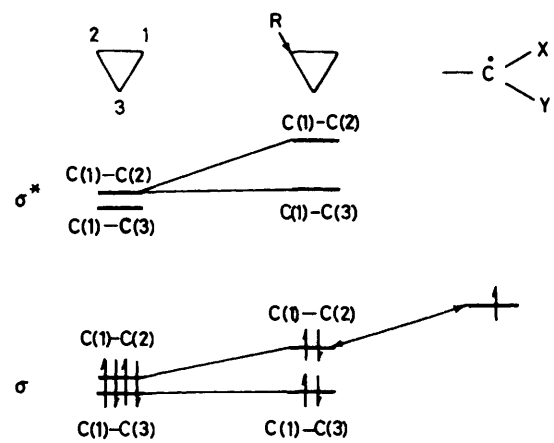


Figure 3. R electron releasing, X and Y electron attracting. SOMO–σC(1)–C(2) interaction

reaction of a trialkyltin hydride (usually tributyltin hydride) with an alkene or an alkyl chloride, by the general procedures we have described previously.[11] The results are given in Table 1.

A mixture of the alkene (**5**) (Scheme 2) and trimethyltin hydride was irradiated at 25 °C with light from a mercury arc filtered through Pyrex glass, and the isomeric composition of the allyltin compounds (**8**) and (**9**) (R = Me) which were formed was determined by ^1H n.m.r. spectroscopy, and g.l.c.; no cyclic reduction product could be detected. The analysis was confirmed by protolysis of the products with HBr, and analysis of the alkenes (**10**) and (**11**) by ^1H and ^{19}F n.m.r., g.l.c.—m.s., and high-resolution m.s. Consistent results were obtained which were independent of the ratio of the initial reagents.

Similar reactions were carried out with tributyltin hydride but the protolysis was carried out directly on the crude mixture of (**8**) and (**9**) (R = Bu), and only the relative yields of the alkenes (**10**) and (**11**) were determined. Again the ratio of (**8**):(**9**) was *ca.* 4:1 at 25 °C, and this ratio increased at −25 °C.

The mechanism of the ring opening is shown in Scheme 2. The effect of temperature on the regioselectivity shows that the preferential formation of the linear product (**9**) is kinetically controlled, and we conclude that the trifluoromethyl substituent in (**6**) is directing the ring-opening to favour the *secondary* alkyl radical (**7**). In contrast, hydrostannation of *trans*-1-methyl-2-vinylcyclopropane under conditions of kinetic control showed a regioselectivity in favour of the *primary* alkyl radical.[11]

Reactions involving the analysis of the products from the

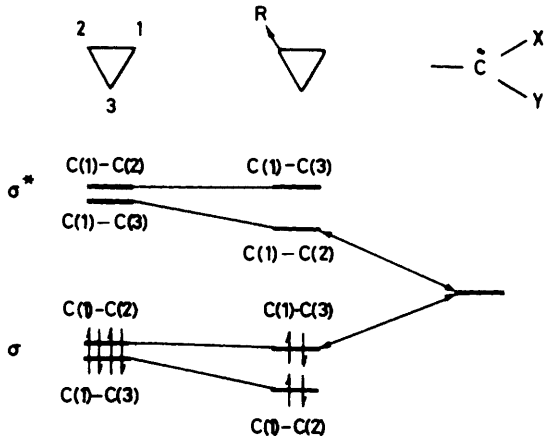


Figure 4. R electron attracting, X and Y electron attracting. Ambiguous SOMO interactions

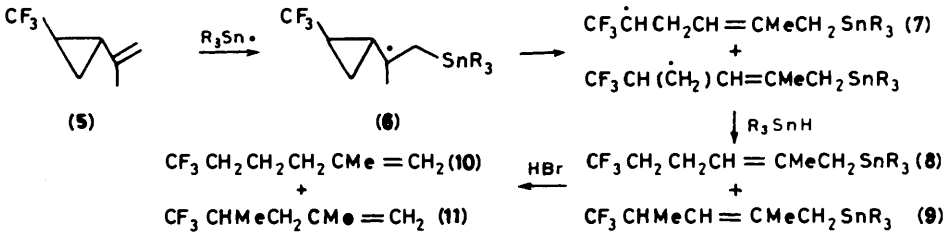
reduction of cyclopropylcarbinyl chlorides (**12**) were carried out by irradiation of the mixture of the chloride and tributyltin hydride with u.v. light at a controlled temperature, and the products were analysed by n.m.r. and g.l.c., in comparison with authentic compounds.[11] The mechanism of the reaction is shown in Scheme 3.

When R = CH_3 and X = Cl, the linear alkene (**17**) was always formed in preference to the branched alkene (**18**). The ratio (**17**):(**18**) decreased from +25 to −25 °C, but then it was little changed down to −80 °C (see Table 1). Further, at this low temperature, the reduction gave 35% of the cyclic product (**16**), and this was wholly of the *trans*-structure. This establishes that the yields of the alkenes (**17**) and (**18**) (*ca.* 60:40) are kinetically controlled, and that the reclosure of the radicals (**14**) and (**15**) to give the *cis*-isomer of (**13**), which could then reopen with a different regioselectivity, introducing some thermodynamic control of products, is insignificant.

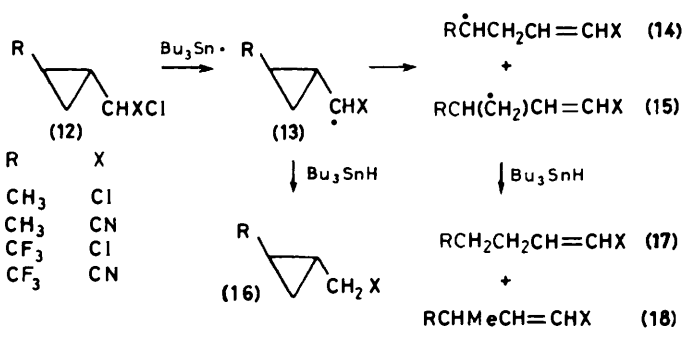
In contrast, the *trans*-2-methylcyclopropylmethyl radical (**13**; R = CH_3, X = H) undergoes ring-opening at 25 °C under conditions of kinetic control to give the corresponding secondary and primary alkenes (**17**) and (**18**) (R = CH_3, X = H) in the reversed ratio of *ca.* 40:60.[9]

Several reductions were carrried out, at −20 °C, of the chloronitrile (**12**; R = CH_3, X = CN), and showed good reproducibility. Analysis of the products by g.l.c., n.m.r., and m.s. showed that the *cis* and *trans* linear alkenes (**17**) were formed in the ratio of 60:40, and there was no evidence for the presence of the branched nitrile (**18**). The reaction conditions were conducive to kinetic control, and it seems likely that ring-opening of the radical (**13**; R = CH_3, X = CN) is regiospecific in favour of the secondary alkyl radical (**14**).

trans-2-Trifluoromethylcyclopropyldichloromethane (**12**; R = CF_3, X = Cl) was reduced with tributyltin hydride at +25 and −25 °C. The progress of the reaction was followed by n.m.r. and g.l.c.–m.s. The relative proportions of the linear and branched alkenes (**17**) and (**18**) (R = CF_3, X = Cl), and of their steric compositions, stayed constant throughout the reaction, and a substantial amount of the *trans* cyclic reduction product



Scheme 2.



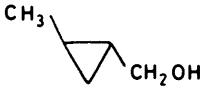
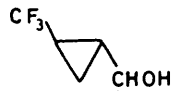
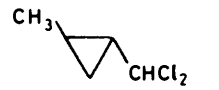
Scheme 3.

(**16**; R = CF_3, X = Cl) was formed even at +25 °C. The absence of *cis*-(**16**) precludes the possibility of thermodynamic control of products, and we conclude that the radical (**13**; R = CF_3, X = Cl) undergoes ring-opening to give preferentially the secondary radical (**14**).

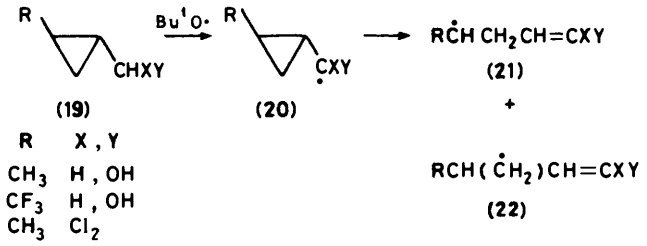
The chloronitrile (**12**; R = CF_3, X = CN) was reduced under a variety of conditions. With a dilute solution of tributyltin hydride in heptane at 25 °C, the cyclic reduction product (**16**; R = CF_3, X = CN) and the linear alkene (**17**; R = CF_3, X = CN) were formed in the ratio of 1:4. At the other extreme, with the neat hydride at −25 °C, the ratio (**16**):(**17**) was 4:1. Under no conditions was the branched alkene (**18**) detected. The relative proportions of *cis*- and *trans*-(**17**) (36:64 at 25 °C in solution, 58:42 at 25 °C, and 57:43 at −25 °C without solvent) are in accord with kinetic control of products in the reactions with no solvent. Again, apparently the ring-opening of the radical is regiospecific in favour of the secondary alkyl radical (**14**; R = CF_3, X = CN).

E.s.r. Spectroscopy.—The experiments involving analysis of products were supplemented by e.s.r. experiments in which the cyclopropylcarbinyl radicals were generated photolytically and monitored spectroscopically. This technique has the advantage that it can readily be carried out at low temperatures where the relative concentrations of the ring-opened radicals are under kinetic control. Unfortunately, a number of the compounds carrying electronegative substituents, which are described here, gave spectra which could not be interpreted with confidence because they were too weak, because either the formation of the initial radicals, or their ring opening, was too slow. All the successful experiments involved photolysis of di-t-butyl peroxide in the presence of the cyclopropyl compound, when the reactions which occur are those shown in Scheme 4. The

Table 2. E.s.r. spectra observed from the reaction of t-butoxyl radicals with cyclopropylcarbinyl compounds[a]

Reactant	T/°C	Radical	Hyperfine coupling constants (G)		
	-99	$CH_3CH(\dot{C}H_2)CH{=}CHOH$	21.7 (2 H_α)	29.4 (H_β)[b]	*ca.* 0.6 (H_γ)[b]
	-130		18.4 (H_α)	12.0 (H_β)	2.0 (H_γ)
	-82	$CF_3\dot{C}HCH_2CH{=}CHOH$	22 (H_α)	30 (3 F and 2 H_β)	
	-57	$CH_3\dot{C}HCH_2CH{=}CCl_2$	22.0 (H_α)	25.0 (5 H_β)	

[a] Cyclopropane solvent. [b] See text.



Scheme 4.

e.s.r. spectra of the radicals which were observed are shown in Table 2.

Photolysis of di-t-butyl peroxide in the presence of *trans*-2-methylcyclopropylmethanol (**19**; R = CH_3, X = H, Y = OH), in cyclopropane gave a strong spectrum of the primary alkyl radical (**22**) at −99 °C. This provides a further example of the anomalous but now familiar regioselectivity which is our present concern. The only unusual feature in the spectrum is the apparent hyperfine coupling to two equivalent γ-H atoms at *ca.* 0.6 G, but this is probably the result of superimposed spectra of *cis*- and *trans*-forms of the radical (**22**) in equal concentrations, with similar *g* values but differing in values of $a(H_\beta)$ by an amount equal to $a(H_\gamma)$.

A similar experiment with *trans*-2-trifluoromethylcyclopropylmethanol (**19**; R = CF_3, X = H, Y = OH) showed the spectrum of the cyclic radical (**20**) at −130 °C, and then, at −82 °C, a rather weak spectrum of the secondary alkyl radical (**21**). Some weaker signals which might be ascribed to the primary alkyl radical (**22**) were also present, but the identity of the major component was unmistakable because of its unusual width.

We conclude that, under the same low temperature conditions a *trans*-2-methyl substituent causes the cyclopropylhydroxymethyl radical to undergo ring-opening to give only the primary alkyl radical, but a *trans*-2-trifluoromethyl substituent has the opposite effect in giving at least principally the secondary alkyl radical.

trans-1-Dichloromethyl-2-methylcyclopropane provided a radical (**20**; R = CH_3, XY = Cl_2) carrying electronegative substituents at the radical centre. At −57 °C, the e.s.r. spectrum showed signals for the secondary alkyl radical (**21**; R = CH_3, XY = Cl_2) and the primary alkyl radical (**22**) could not be detected.

Table 3. Calculated ionisation potentials, electron affinities, and electronegativities of radicals (eV)

	I.P.	E.A.	ζ[a]
CH_3·	10.40	0.39	5.40
CH_2Cl·	9.95	1.10	5.53
$CHCl_2$·	9.75	1.91	5.83
CCl_3·	9.74	2.56	6.15

[a] $\zeta = \frac{1}{2}$(I.P. + E.A.)

Discussion

Entry 1 in Table 1 and entries 1 and 2 in Table 2, show that the replacement of a *trans*-CH_3 substituent by *trans*-CF_3 in a cyclopropylcarbinyl radical changes the regioselectivity so that the secondary rather than the primary alkyl radical is formed preferentially.

This is in accord with the predictions of an extension of our model, as shown in Figure 2. Electron attraction by the trifluoromethyl substituent will place the energy of the C(1)–C(2) σ* orbital below that of the C(1)–C(3) σ* orbital. The SOMO–C(1)–C(2) σ* interaction will now be dominant, resulting in cleavage of the C(1)–C(2) bond and formation of the secondary alkyl radical, as illustrated.

Entry 2 of Table 1 and entry 3 of Table 2 show that when the substituent is held constant at CH_3, introduction of one or two chloro groups at the radical centre inverts the regioselectivity so that the secondary alkyl radical is formed preferentially.

There is some ambiguity regarding the relative SOMO energy levels of alkyl, chloroalkyl, and dichloroalkyl radicals: Table 3 shows calculated values for the ionisation potentials (I.P.) and electron affinities (E.A.) and the derived Mulliken electronegativities (ζ).[13]

Although the values of the ionisation potentials of the radicals decrease with progressive chlorination, the electron affinities increase, and more markedly, so that the electronegativities show a net increase.

If it may be assumed that chlorination at the radical centre lowers the energy of the SOMO, the inversed regioselectivity may be rationalised in terms of Figure 3. The interaction is now principally with the occupied C(1)–C(2) σ orbital, resulting in the cleavage of this bond, and the formation of the secondary alkyl radical. In contrast the net effect of a hydroxy group is to reduce the electronegativity by conjugative electron release ($HOCH_2$·, I.P. *ca.* 7.5 eV); the radical interacts principally with the C(1)–C(3) σ* orbital, and ring-opening gives the primary alkyl radical.

To overcome the ambiguity of the effect of a chloro substituent on the SOMO energy level, the regioselective effect of a cyano substituent was investigated (entry 3, Table 1). The SOMO energy level will now be lower, and the regiospecific ring-opening to give the linear product *via* the secondary alkyl radical can be understood in terms of Figure 3.

The orbital interactions which may occur when both the radical centre and the ring substituent are electronegative are illustrated in Figure 4. The SOMO energy level will now be placed between the C(1)–C(3) σ and C(1)–C(2) σ* energy level, but which of the two possible interactions will predominate will depend on the degree to which C(1)–C(2) σ* and the SOMO are lowered, and will not be predictable on the basis of our qualitative model. Entry 4 of Table 1 indicates that the effect of the CF_3 substituent in lowering C(1)–C(2) σ* offsets the effect of an α-Cl group in lowering the SOMO energy, and the principal interaction is that between C(1)–C(2) σ* and the SOMO. Entry 5, Table 1, implies that the effect of an α-cyano group is still not sufficient to reduce the SOMO energy to the point where interaction with the C(1)–C(3) σ orbital is dominant: the principal interaction is still with the C(1)–C(2) σ* orbital, and ring opening occurs to give only the secondary alkyl radical.

It is notable that both these last two reactions give an appreciable amount of cyclic product, implying that when both the radical centre and the ring substituent are electronegative, the ring opening is relatively slow. It is difficult to make direct comparisons, because the relative reactivity of different electronegative alkyl radicals with tributyltin hydride is not known, but it seems possible that regiospecificity of the ring-opening of the (*trans*-2-trifluoromethylcyclopropyl)cyanomethyl radical may be associated with a particularly slow ring-opening reaction.

Conclusions.—We conclude that the general model which we proposed to explain the regioselectivity of ring-opening of a cyclopropylalkyl radical carrying a *trans*-2-alkyl substituent is also capable of accommodating the regioselectivity which is observed when the radical centre and/or the substituent is rendered electronegative.

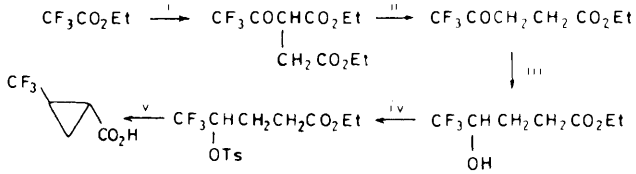
Our model however is highly qualitative, and its limitations should be recognised. First, we have no quantitative knowledge of the energy levels which are involved. Second, we have considered only the energy levels, whereas a proper treatment should also take into consideration the coefficients of the atomic orbitals.[14] Third, when electronegative substituents are present, some of the ring-opening reactions are relatively slow, and the frontier orbital approach is less reliable with reactions which involve a late transition state.[14]

Experimental

Preparation of Materials.—trans-2-*Trifluoromethylcyclopropanecarboxylic acid.* The precursor of all the trifluoromethylcyclopropyl compounds was *trans*-2-trifluoromethylcyclopropanecarboxylic acid,[15] the preparation of which was modified to reduce the parasitic formation of lactone in the decarboxylation step (Scheme 5). In the original preparation, the succinate was treated with sulphuric acid to give 3-trifluoroacetylpropionic acid which was then treated with diazomethane to give the methyl ester in 38% overall yield. If the decarboxylation is carried out using boric acid, the ethyl ester is formed in 62% yield; the reaction probably involves an intermediate chelated boron carboxylate.[16]

The crude diethyl trifluoroacetylsuccinate, b.p. 80—130 °C at 1 mmHg, was obtained by Tatlow's method in 75% yield.[17]

A mixture of this succinate (80 g, 0.3 mol) and boric acid (19 g, 0.3 mol) was heated slowly to 170 °C, when the ethanol was eliminated gradually as it was formed. After this was complete (*ca.* 3 h), the contents of the flask were poured over ice. The product was extracted with toluene, and worked up to give ethyl 3-trifluoroacetylpropionate (36 g, 62%), b.p. 66 °C at 10 mmHg; ν 1 740 and 1 765 cm^{-1} (C=O); δ (CCl_4) 1.22 (3 H, t, CH_3), 2.42—3.12 (4 H, m, CH_2CH_2), and 4.06 (2 H, q, CH_2CH_3).



Scheme 5. *Reagents:* i, $CH_2(CO_2Et)_2$–NaOEt; ii, H_3BO_3; iii, H_2–PtO_2; iv, *p*-$CH_3C_6H_4SO_2Cl$; v, Bu^{t}OK–Me_2SO

This keto ester in ether was hydrogenated at atmospheric pressure in the presence of platinum oxide (0.1 g) giving ethyl 4-hydroxy-5,5,5-trifluoropentanoate in 95% yield.

The absence of a band at 1 815 cm^{-1} in the i.r. spectrum confirmed the absence of lactone, δ (CCl_4) 1.25 (3 H, t, CH_3), 1.65—2.15 (2 H, m, HOCHCH_2), 2.32—2.75 (2 H, m, CH_2CO_2Et), and 3.55—4.35 (3 H, q, CH_2CH_3 and m, CHOH).

Reaction of the hydroxy ester with toluene-*p*-sulphonyl chloride gave the toluene-*p*-sulphonate as a viscous oil which solidified at −14 °C, δ (CCl_4) 1.25 (3 H, t, CH_3), 1.70—2.30 (2 H, m, CH_2CHOTs), 2.32—2.88 (5 H, s, $CH_3C_6H_4$ and m, CH_2CO_2Et), 4.12 (2 H, q, CH_2CH_3), 4.72—5.38 (1 H, m, CHOTs), and 7.18—7.98 (4 H, m, C_6H_4).

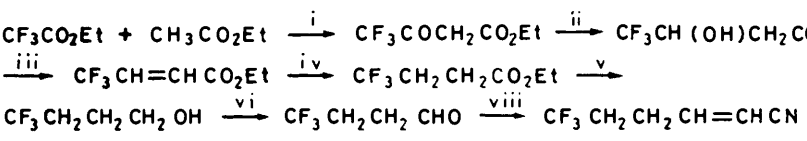
Treatment of the tosylate with potassium t-butoxide in dimethyl sulphoxide gave *trans*-2-trifluoromethylcyclopropanecarboxylic acid (65%), b.p. 52 °C at 10^{-2} mmHg; ν 1 700 (CO) and 1 020 (ring) cm^{-1}; δ (CCl_4) 1.2—1.7 (2 H, m, ring CH_2), 1.82—2.55 (2 H, m, ring CH), and 13 (1 H, s, CO_2H); *m/e* 154 (14%), 85(100), 77(10), 69(20), 64(13), 57(11), 56(10), 42(10), 41(42), 39(21), 31(10), and 29(60).

The *trans*-structure was confirmed by ^1H n.m.r., at 400 MHz, of the acid. Simulation of the spectrum showed that $^3J(CF_3CH$–$CHCO_2H) = 4$ Hz which is characteristic of coupling between *trans*-cyclopropyl protons.[18]

trans-2-*Trifluoromethylcyclopropylmethanol.* A solution of *trans*-2-trifluoromethylcyclopropanecarboxylic acid (12 g, 0.078 mol) in ether (50 cm^3) was added dropwise to a suspension of lithium aluminium hydride (4 g, 0.1 mol) in ether. The mixture was heated under reflux for 16 h, then worked up to yield the chromatographically pure alcohol in 75% yield, b.p. 140—140 °C at 760 mmHg; δ(CCl_4) 0.6—1.1 (2 H, m, ring CH_2), 1.2—1.9 (2 H, m, ring CH), and 3.5 (2 H, d, CH_2OH, *J* 5 Hz); *m/e* 140(0%), 123(3), 77(21), 69(5), 44(100), 43(23), 39(11), and 31(17).

trans-2-*Trifluoromethylcyclopropanecarbaldehyde.* The above alcohol (5 g, 0.035 mol) in dichloromethane (10 cm^3) was added in a single portion at room temperature to a mixture of pyridinium chlorochromate (11 g, 0.051 mol) in dichloromethane (60 cm^3).[19] The mixture turned black; it was stirred for 2 h, then the tar was extracted with ether. The ethereal solution was purified through a small column of Florisil, yielding the aldehyde (4.2 g, 85%), δ(CCl_4) 1.1—1.65 (2 H, m, CH_2), 1.82—2.6 (2 H, m, ring CH), 9.45 (1 H, d, CHO, *J* 3 Hz); *m/e* 138(22%), 137(16), 109(13), 91(17), 90(23), 89(25), 69(100), 64(31), 59(25), 51(13), 41(47), and 39(78).

trans-1-*Chlorocyanomethyl*-2-*trifluoromethylcyclopropane.*[20,21] An equimolar mixture of the above aldehyde (6.1 g, 0.044 mol) and of aqueous sodium hydrogen sulphite (22 g of a solution of *d* 1.24) was stirred for some hours at room



Scheme 6. *Reagents:* i, NaOEt; ii, $NaBH_4$; iii, P_2O_5; iv, H_2–PtO_2; v, $LiAlH_4$; vi, [O]; vii, $(EtO)_2POCH_2CN$

temperature. To this solution of the hydrogen sulphite compound at 0 °C, a solution of sodium cyanide (5.7 g, 0.11 mol) in water (21 cm^3) was added. The mixture was stirred for 3 h, then extracted with ether to give the cyanohydrin (6.8 g, 93%).

This cyanohydrin (6.8 g, 0.04 mol) and $POCl_3$ (30 cm^3, 0.32 mol) were mixed in pyridine at 0 °C, then heated under reflux for 20 min. The mixture was poured over ice, then extracted into ether, and acidified to pH 2 with 20% HCl, yielding the chlorocyanide (2.5 g, 33%). G.l.c. analysis [10% Carbowax 20M on Chromosorb W (aw DMCS) 80—100; 3 mm × 2 m; N_2 at 20 cm^3 min^{-1}; 130 °C] showed the presence of two diastereoisomers. The C≡N group could not be distinguished in the i.r. spectrum, δ(CCl_4) 0.95—1.58 (2 H, m, CH_2), 1.6—2.2 (2 H, m, ring CH), 4.45 and 4.47 (1 H, 2 d, CHClCN, *J* 7.5 Hz).

trans-1-*Bromocyanomethyl*-2-*trifluoromethylcyclopropane*. This was prepared in the same way as the chloro compound above, but using $POBr_3$. The yield was 7%. The presence of two diastereoisomers was confirmed by g.l.c., and by m.s., δ(CCl_4) 0.95—1.6 (2 H, m, CH_2), 1.6—2.2 (2 H, m, ring CH), and 4.35 (1 H, 2 d, CHBrC*H*, *J* 7.5 Hz). The mass spectra of the chloro- and bromo-cyanomethyl-2-trifluoromethylcyclopropanes are identical.

trans-1-*Cyanomethyl*-2-*trifluoromethylcyclopropane*. *trans*-2-Trifluoromethylcyclopropylmethanol was treated with toluene-*p*-sulphonyl chloride and pyridine at 0 °C for 48 h to give the tosylate in 36% yield as a viscous liquid, δ(CCl_4) 0.7—1.25 (2 H, m, ring CH_2), 1.25—1.80 (2 H, m, ring CH), 2.45 (3 H, s, CH_3), 3.92 (2 H, d, CH_2O, *J* 6 Hz), and 7.25—7.82 (4 H, m, C_6H_4).

This tosylate (2.5 g, 0.008 mol) and sodium cyanide (0.6 g, 0.011 mol) in DMSO (28 cm^3) were heated at 90 °C for 5 h.[22] Hydrolytic work-up yielded the nitrile (40%), b.p. 75 °C at 30 mmHg, which was shown to be pure by g.l.c., ν 2 250 cm^{-1} (weak; CN); δ(CCl_4) 0.65—2.0 (3 H, m, ring protons), 2.45 (2 H, d, CH_2CN, *J ca.* 6 Hz); *m/e* 149(7%), 122(12), 109(100), 103(18), 102(16), 89(36), 80(15), 77(39), 69(10), 59(22), 54(15), 53(42), and 40(32).

trans-1-*Dichloromethyl*-2-*trifluoromethylcyclopropane*. Phosphorus pentachloride (4.5 g, 0.021 mol) was added to 2-trifluoromethylcyclopropanecarbaldehyde (2.7 g, 0.019 mol) in ether (3 cm^3) at 0 °C, and the mixture was stirred for 2 h at 0 °C to eliminate hydrogen chloride. The product was extracted into pentane, and isolated by preparative g.l.c. in 7% yield (30% Castorwax on Chromosorb P60—80; 9.5 mm × 2 m; N_2 at 200 cm^3 min^{-1}; 80 °C), δ(CCl_4) 0.98—1.55 (2 H, m, CH_2), 1.55—2.35 (2 H, m, ring CH), and 5.58 (1 H, d, $CHCl_2$, *J* 6 Hz); *m/e* 192(0%), 157(25), 137(10), 101(14), 98(63), 96(100), 93(12), 83(14), 77(36), 69(11), 64(16), 62(51), and 51(17).

trans-1-*Isopropenyl*-2-*trifluoromethylcyclopropane*. 2-Trifluoromethylcyclopropanecarboxylic acid (3.4 g, 0.22 mol) in ether was treated with methyl-lithium (0.04 mol) in ether for 12 h, yielding 2-trifluoromethylcyclopropyldimethylcarbinol (45%). Dehydration with phosphoric acid gave the alkene in 15% yield, δ(CCl_4) 0.75—1.85 (4 H, m, ring H), 1.65 (3 H, m, CH_3), and 4.65 (2 H, m, CH_2=C); *m/e* 150(25%), 135(30), 115(32), 81(100), 79(29), 67(45), 53(61), and 51(29).

trans-2-*Methylcyclopropylcarbaldehyde*. This compound was the precursor of the methylcyclopropyl reactants. Crotonaldehyde was reduced with lithium aluminium hydride to crotyl alcohol (84%), b.p. 117—120 °C. This was subjected to Simmons–Smith methylenation using a zinc–copper couple giving *trans*-2-methylcyclopropylmethanol (73%), b.p. 60 C at 30 mmHg; δ(CCl_4) 0.20—0.80 (4 H, m, ring H), 1.04 (3 H, d, CH_3), and 3.31 (2 H, d, C*H*$_2$OH).

The alcohol was oxidised by the procedure described above for the trifluoromethyl compound, giving *trans*-2-methylcyclopropanecarbaldehyde (68%), b.p. 100 °C; δ(CCl_4) 0.52—1.8 (7 H, m, ring H and CH_3) and 8.85 (1 H, d, CHO).

trans-1-*Dichloromethyl*-2-*methylcyclopropane*. The preparation was carried out by the method described above for the trifluoromethyl analogue. The crude product was a mixture of *trans*-1-dichloromethyl-2-methylcyclopropane (*ca.* 80%) and of *cis*- and *trans*-1,4-dichloropent-1-ene (*ca.* 20%). This was separated by g.l.c. (30% Castorwax on Chromosorb P60—80; 9.5 mm × 2 m; N_2 at 200 cm^3 min^{-1}; 80 °C), giving the dichloromethyl compound in 11% yield, δ(CCl_4) 0.38—1.55 (7 H, m, ring H and CH_3) and 5.15 (1 H, d, $CHCl_2$, *J* 9 Hz); *m/e* 142(2%), 140(13), 138(21), 103(26), 89(20), 75(100), 67(28), 65(21), 63(66), 55(16), and 27(34).

trans-1-*Chlorocyanomethyl*-2-*methylcyclopropane*. The same method was used as described above for the trifluoromethyl compounds, except that, in the final stage, the pyridine solution was not heated under reflux, but was shaken at room temperature for 2 h. The cyanohydrin was obtained from the aldehyde in 83% yield, δ(CCl_4) 0.3—1.25 (7 H, m, ring H and CH_3) and 4.05 and 4.08 [1 H, 2 d, C*H*(OH)CN]. From this, the crude chloronitrile was obtained in 17% yield. This was purified (2 diastereoisomers) by g.l.c. (30% Castorwax on Chromosorb P60—80; 9.5 mm × 2 m; N_2 at 200 cm^3 min^{-1}; 110 °C), giving the pure product in 3% yield, δ(CCl_4) 0.42—1.42 (7 H, m, ring H and CH_3) and 4.16 and 4.18 (1 H, 2 d, CHClCN, *J* 7.5 Hz); *m/e* 94(35%), 67(100), 66(33), 63(17), 55(61), 42(16), 41(30), 39(40), and 27(38).

1-*Cyano*-5,5,5-*trifluoropent*-1-*ene*. This compound was required for identifying the products of the ring-opening of the 2-trifluoromethylcyclopropylcyanomethyl radical, and was prepared by the sequence in Scheme 6.

The condensation of ethyl trifluoroacetate and ethyl acetate was carried out by the published method,[23] but the product was isolated by a classic hydrolysis, followed by azeotropic dehydration.

Sodium (14 g) was dissolved in absolute ethanol; to this was added ethyl trifluoroacetate (63 g, 0.45 mol) and ethyl acetate (40 g, 0.45 mol). The mixture was heated under reflux for 48 h at 90 °C, then hydrolysed with the *minimum* of 10N-H_2SO_4, yielding a mixture of the β-keto ester and its hydrate, b.p. 42—55 °C at 30 mmHg. This was dehydrated in boiling benzene for 12 h, using a Dean and Stark water separator, giving the enol form of the β-keto ester in 30% yield, b.p. 42 °C at 30 mmHg: $CF_3C(OH)_2CH_2CO_2Et$, δ(CCl_4) 1.25 (3 H, t, CH_3), 2.68 (2 H, s, CH_2CO), and 4.15 (2 H, q, C*H*$_2$CH$_3$); $CF_3C(OH)$=$CHCO_2Et$, δ(CCl_4) 1.25 (3 H, t, CH_3), 4.15 (2 H, q, C*H*$_2$CH$_3$), 5.50 (1 H, s, =CH), and 14 (1 H, s, OH).

Reduction of this keto ester with sodium borohydride[24] gave ethyl 3-hydroxy-4,4,4-trifluorobutanoate (68%), b.p. 93 °C at 30 mmHg; δ(CCl_4) 1.25 (3 H, t, CH_3), 2.65 (2 H, d, C*H*$_2CO_2$Et, *J* 7.5 Hz), 3.98—4.75 (1 H, m, C*H*OH), and 4.15 (2 H, q, C*H*$_2$CH$_3$).

Dehydration with phosphorus pentaoxide[25] gave the unsaturated ester in 80% yield, b.p. 112 °C; δ(CCl_4) 1.30 (3 H, t, CH_3), 4.22 (2 H, q, CH_2), and 6.22—7.12 (2 H, m, CH=CH).

This unsaturated ester (26 g, 0.158 mol) in dry ether was

reduced with hydrogen at 4 atm. pressure, over platinum oxide, for 8 h, giving ethyl 4,4,4-trifluorobutyrate in 84% yield, δ(CCl_4) 1.22 (3 H, t, CH_3), 1.90—2.70 (4 H, m, CH_2CH_2), and 4.05 (2 H, q, CH_2CH_3).

The ester (22 g, 0.125 mol) was reduced in ether (50 cm^3) with lithium aluminium hydride (3.5 g, 0.09 mol), under reflux for 3 h, giving 4,4,4-trifluorobutanol in 53% yield, b.p. 122 °C; δ(CCl_4) 1.55—2.70 (4 H, m, CH_2CH_2) and 3.60 (2 H, t, CH_2OH).

Oxidation with pyridinium chlorochromate as described above gave 4,4,4-trifluorobutyraldehyde (15%), b.p. 95 °C; δ(CCl_4) 2.0—2.95 (4 H, m, CH_2CH_2), and 9.70 (1 H, t, CHO).

To a suspension of sodium hydride (0.2 g, 0.008 mol) in anhydrous dimethoxyethane (10 cm^3), a solution of diethylphosphonoacetonitrile (1.41 g, 0.008 mol) was added dropwise at 0 °C under argon; the temperature within the flask was *ca.* 4—5 °C. The mixture was stirred for 20 min, then a solution of the aldehyde (0.95 g, 0.008 mol) in a little solvent was added at 0 °C.[26] The mixture was stirred at room temperature for 30 min, then worked up to give 0.7 g of a crude mixture of *cis*- and *trans*-1-cyano-5,5,5-trifluoropent-1-ene together with an unidentified impurity which could be removed by distillation at 30 mmHg; yield, 13%. G.l.c. analysis [10% Carbowax on Chromosorb W (aw DMCS) 80—100; 9.5 mm × 2 m; N_2 at 20 cm^3 min^{-1}; 110 °C] and ^1H n.m.r. spectroscopy at 270 MHz indicated the *cis*-isomer (60%; ^3J *ca.* 9 Hz) and the *trans*-isomer (40%; ^3J *ca.* 16 Hz); under the above conditions, the *trans*-isomer is eluted first, δ(CCl_4; 270 MHz) 1.36—1.98 (2 H, m, CF_3CH_2), 2.07—2.66 (2 H, m, $CF_3CH_2CH_2$), 4.57—4.7 (1 H, m, $CH_2CH_B{=}CH_A$), 5.83—6.00 (1 H, m, $CH_2CH_B{=}CH_A$) [$J(H_A{-}H_B)$ 16.5, $J(H_B{-}CH_2)$ 6.5, $J(H_A{-}CH_2)$ 2 Hz]; *cis*-isomer, δ 4.77—4.93 (1 H, m, $CH_2CH_B{=}CH_A$) and 5.57—5.75 (1 H, m, $CH_2CH_B{=}CH_A$) [$J(H_A{-}H_B)$ 10, $J(H_B{-}CH_2)$ 7.5, $J(H_A{-}CH_2)$ 1 Hz].

The structures were confirmed by g.l.c.—m.s.: *trans*, *m/e* 149(65%), 129(26), 122(63), 109(26), 102(100), 80(55), 77(20), 69(33), 66(72), 65(24), 64(41), 54(22), 53(77), 52(27), 51(30), 41(15), 39(61), and 27(33); *cis*, *m/e* 149(62%), 129(23), 122(60), 109(26), 102(96), 80(46), 77(19), 69(32), 66(100), 65(11), 64(42), 54(20), 52(24), 51(28), 41(19), 39(65), and 27(33).

Hydrostannation of trans-1-*Isopropenyl*-2-*trifluoromethylcyclopropane*.—A typical experiment was as follows. A mixture of trimethyltin hydride (0.23 g, 1.3 mmol) and of the alkene (0.20 g, 1.3 mmol) under nitrogen in an n.m.r. tube was irradiated with u.v. light from a Philips HPK-125 mercury arc. The progress of the reaction was followed by g.l.c. [dual columns of Carbowax 20 M 10%; Chromosorb W (aw DMCS) 80—100; 3 mm × 5 m; N_2 at 20 cm^3 min^{-1}; 95 °C], or by n.m.r. The branched allylic product (**9**) was eluted first, and no cyclic product was detected: $CF_3CH_2CH_2CH{=}C(CH_3)CH_2SnMe_3$ (*Z* + *E*) 80%, $CF_3CH(CH_3)CH{=}C(CH_3)CH_2SnMe_3$ (*Z* + *E*) 20%. This regioselectivity was independent of the concentration of the hydride.

A mixture of the four isomers showed δ (CCl_4; 60 MHz) 0.15 (s, Me_3Sn), 0.20 (9 H, s, Me_3Sn), 1.24 (3 H, d, CF_3CHCH_3, *J* 7.5 Hz), 1.55—1.95 (5 H, m, $CH_3C{=}$ and CH_2SnMe_3), 2.05—2.5 (4 H, m, $CF_3CH_2CH_2$), 2.65—3.0 (1 H, m, CF_3CHCH_3), and 4.65—5.25 (1 H, m, CH=C). At 90 MHz, four separate singlets for the Me_3Sn groups could be distinguished.

The structures of the organotin adducts were confirmed by protolysis as shown in Scheme 2. Hydrogen bromide gas was passed directly into the n.m.r. tube and the progress of the reaction was monitored spectroscopically. The crude product showed δ ($CDCl_3$; 90 MHz) 0.56 (9 H, s, Me_3SnBr), 1.1 (3 H, d, CF_3CHCH_3, *J* 6 Hz), 1.66 (3 H, br s, $CH_3C{=}$), 1.84—2.52 [8 H, m, $CF_3(CH_2)_3$ and $CF_3CH(CH_3)CH_2$], and 4.56—4.84 (2 H, m $CH_2{=}C$).

By g.l.c., the branched isomer $CF_3CH(CH_3)CH_2C(CH_3){=}CH_2$ was eluted first (15% XF 1 150 on Chromosorb P 100—120; 3 mm × 2 m; N_2 at 20 cm^3 min^{-1}; room temperature); *m/e* [$CF_3CH_2CH_2CH_2C(CH_3){=}CH_2$], 152(19%), 137(9), 69(54), 56(100), 55(90), 41(69), and 39(39); ($CF_3CHMeCH_2CMe{=}CH_2$) 152(11%), 83(10), 56(100), 55(90), 41(26), and 39(25).

As g.l.c.—m.s. did not allow unambiguous identification of the isomers, the assignments were confirmed by high-resolution m.s.

The peak at *m/e* 83 in the spectrum of the mixture was resolved into a doublet under high resolution, *m/e* 83.010 855 ($C_2H_2F_3$), and 83.086 071 (C_6H_{11}). The former ion is specific to the linear isomer (**10**), originating from simple fragmentation to give the ion $CF_3CH_2^+$; the same scission of the branched isomer would give the ion $CF_3\overset{+}{C}HCH_3$ (*m/e* 97). The latter ion is non-specific, arising from both isomers by the reaction $M^{+\cdot} \longrightarrow C_6H_{11}^+ + CF_3^{\cdot}$.

Having differentiated the two isomers, the fragmentation patterns were determined at high resolution (4 000), separating the fluorinated and the purely hydrocarbon ions. The ion $C_2H_2F_3^+$ showed effectively only a single peak corresponding to the linear isomer, but the trace for the ion $C_6H_{11}^+$ showed two peaks for the two isomers. We conclude that the branched isomer (**11**) is eluted first on the chromatogram. Further confirmation is provided by the fact that the most intense peak corresponds to the more important fragmentation to give the secondary alkyl cation.

The ^{19}F n.m.r. spectrum of the mixed isomers (**10**) and (**11**) was recorded ($CDCl_3$; 75.26 MHz); no internal reference was used, and only differences in chemical shifts are significant. The spectrum showed a broad band (*A*) with the general appearance of a triplet, with δ 6 658 Hz, a doublet (*B*) δ 5 940 Hz (*J* 11 Hz), and a doublet (*C*) δ 5 414 Hz (*J* 11 Hz), relative intensities *A* 80%, *B* 18%, *C* 2%. The band (*A*) is attributed to the linear olefin (**10**) and the doublet (*B*) to the branched olefin (**11**). We believe that the small doublet (*C*) may correspond to a secondary product resulting from either acid-catalysed isomerisation of the olefin, or addition of HBr to the double bond.

Reduction of Cyclopropylcarbinyl Chlorides.—Unless otherwise stated, the reductions were carried out by irradiation, at various temperatures, of an equimolar amount (*ca.* 1 mmol) of the cyclopropyl derivative and the tin hydride, using a Philips HPK 125 lamp. The reaction mixture was always prepared by adding the cyclopropyl compound to the hydride at 0 °C.

For experiments at room temperature, the mixture was prepared directly in an n.m.r. tube or small ampoule, and kept at *ca.* 25 °C in a current of air. In all these reactions, the yields were essentially quantitative (n.m.r. and g.l.c.).

For reactions at −20 °C, cold methanol was circulated around a double-walled cell. Again the yields were practically quantitative. A slight excess of hydride (*ca.* 1.5 mmol) was used, and the excess was decomposed by addition of a drop of carbon tetrachloride before the analysis.

The reactions at −80 °C were carried out in a brass cell fitted with a quartz window, and cooled in solid carbon dioxide. Under these conditions, the reaction is not complete, and the excess of the hydride (*ca.* 2 mmol) was decomposed by addition of the minimum amount of carbon tetrachloride before analysis. The overall yield was then estimated using toluene as an internal standard.

(1) trans-1-*Dichloromethyl*-2-*methylcyclopropane*. The reduction was essentially complete at +25 and −25 °C, but only 40—45% complete at −80 °C. For the reactions at +25 °C, the progress of the reaction was followed by n.m.r. and g.l.c. (Si DC 550 15% on Chromosorb W 80—100; 3 mm × 3 m; N_2 at 20 cm^3 min^{-1}; 50 °C). A small variation in the selectivity was observed as the reaction progressed.

A reference sample of 1-chloropent-1-ene (*cis* + *trans*) was prepared by irradiating a mixture of 1,4-dichloropent-1-ene and

tributyltin hydride for 14 h. The first peak to be eluted by g.l.c. was identified as the *trans*-isomer on the basis of its n.m.r. spectrum at 270 MHz. The dichloropentene was obtained as a by-product from the purification of 1-dichloromethyl-2-methylcyclopropane by preparative g.l.c.

Under our g.l.c. conditions, the branched alkenes were eluted first. At 25 °C, the relative proportions of the alkenes in the sequence of their retention times was *trans*-$Me_2CHCH{=}CHCl$ 12%; *cis*-$Me_2CHCH{=}CHCl$ 14%; *trans*-$MeCH_2CH_2CH{=}CHCl$ 47%; *cis*-$MeCH_2CH_2CH{=}CHCl$ 27% (total yield 100%). No 1-chloromethyl-2-methylcyclopropane was present.

The assignments were confirmed by n.m.r. and g.l.c.—m.s. studies on the volatile product obtained from several reductions at 25 °C: δ ($CDCl_3$; 90 MHz) 0.8—1.1 [9 H, m, CH_3CH_2 and $(CH_3)_2CH$)], 1.02 (6 H, d, $(CH_3)_2CH$, *J* 6 Hz), 1.2—1.7 (2 H, m, $CH_3CH_2CH_2$), 1.94—2.35 [3 H, m, $CH_3CH_2CH_2$ and $(CH_3)_2CH$], and 5.45—6.25 (2 H, m, CH=CH); *m/e* (*trans*-$Me_2CHCH{=}CHCl$) 106(6%), 104(13), 91(11), 89(32), 69(84), 67(10), 53(100), 51(19), 42(90), 41(61), 39(40), and 27(45); (*cis*-$Me_2CHCH{=}CHCl$) 106(6%), 104(16), 91(13), 89(33), 69(92), 67(10), 53(100), 51(20), 42(91), 41(61), 39(40), and 27(44); (*trans*-$MeCH_2CH_2CH{=}CHCl$) 106(7%), 104(18), 77(9), 75(28), 69(10), 67(8), 53(16), 42(100), 41(40), 39(52), 29(19), and 27(32); (*cis*-$MeCH_2CH_2CH{=}CHCl$) 106(7%), 104(21), 77(14), 75(40), 69(10), 67(8), 53(16), 42(100), 41(40), 39(57), 29(20), and 27(33); (1-chloromethyl-2-methylcyclopropane) 106(2%), 104(7), 69(38), 68(19), 67(10), 63(15), 55(100), 53(21), 42(57), 41(71), 39(36), and 27(27).

(2) trans-1-*Chlorocyanomethyl*-2-*methylcyclopropane*. Several reductions were carried out at −20 °C and showed good reproducibility. The progress of the reaction was followed by n.m.r and g.l.c. [Carbowax 20 M 10% on Chromosorb W (aw DMCS) 80—100; 3 mm × 2 m; N_2 at 20 cm^3 min^{-1}; 90 °C]. Both the regioselectivity and the *cis*/*trans* ratio remained constant during the course of the reaction. The n.m.r. spectra (270 MHz) of several drops of the volatile organic product (60% yield at 30 mmHg) enabled the order of elution of the isomeric 1-cyanopent-1-enes to be determined: the *cis* isomer was eluted first: δ(C_6D_6; 270 MHz) (*cis*-$CH_3CH_2CH_2CH_B{=}CH_ACN$) 0.83 (3 H, t, CH_3CH_2), 1.07—1.25 (2 H, m, $CH_3CH_2CH_2$), 2.07—2.20 (2 H, m, $CH_2C{=}$), 4.6—4.8 (1 H, m, H_B), 5.67—5.80 (1 H, m, H_A) [$J(H_A{-}H_B)$ 11, $J(H_A{-}CH_2)$ 1.5, $J(H_B{-}CH_2)$ 8, $J(CH_2{-}CH_2)$ 7.5 Hz]; (*trans*-$CH_3CH_2CH_2CH_B{=}CH_ACN$) 0.69 (3 H, t, CH_3CH_2), 1.03—1.07 (2 H, m, $CH_3CH_2CH_2$), 1.46—1.62 (2 H, m, $CH_2C{=}$), 4.6—4.8 (1 H, m, H_B), 6.06–6.19 (1 H, m, H_A) [$J(H_A{-}H_B)$ 17, $J(H_A{-}CH_2)$ 2, $J(H_B{-}CH_2)$ 6, $J(CH_2{-}CH_2)$ 7.5 Hz].

(3) trans-1-*Dichloromethyl*-2-*trifluoromethylcyclopropane*. Reductions were carried out at room temperature and at −20 °C, and followed by n.m.r. and g.l.c. (Si DC 550 15% on Chromosorb W 80—100; 3 mm × 3 m; N_2 at 20 cm^3 min^{-1}; 100 °C). The relative amounts of the branched and linear alkenes, and their stereochemistries, remained constant throughout the reaction. For each pair of alkenes (branched and linear) we assume that the *trans*-isomer is eluted first, by analogy with our previous results. *trans*-1-Chloromethyl-2-trifluoromethylcyclopropane was prepared for reference purposes by treating the corresponding alcohol with pyridine and thionyl chloride; the *cis*-isomer was absent from the reduction products. In the order of elution the compounds formed were *trans*-$CF_3CHMeCH{=}CHCl$ 14%, *cis*-$CF_3CHMeCH{=}CHCl$ 4%, *trans*-$CF_3CH_2CH_2CH{=}CHCl$ 60%, and *cis*-$CF_3CH_2CH_2CH{=}CHCl$ 22%; *m/e* (*trans*-$CF_3CHMeCH{=}CHCl$) 160(12%), 158(37), 143(18, $[M-CH_3]^+$), 123(8), 103(15), 91 and 89(35 and 100) $[M-CF_3]^+$), 77(12), 69(18), 59(12), 53(61), 51(15), and 27(21); (*cis*-$CF_3CHMeCH{=}CHCl$) 160(10%), 158(31), 143(17; $[M-CH_3]^+$), 123(7), 103(15), 91 and 89(34 and 100, $[M-CF_3]^+$), 77(11), 69(26), 59(20), 53(62), 51(19), and 27(25); (*trans*-$CF_3CH_2CH_2CH{=}CHCl$) 160(16%), 158(48), 123(38), 103(23), 77 and 75(39 and 100, allylic cleavage), 69(8), 59(60), 53(19), 39(31), and 27(16); (*cis*-$CF_3CH_2CH_2CH{=}CHCl$) 160(12%), 158(39), 123(28), 103(19), 77 and 75(38 and 100, allylic cleavage), 69(8), 59(50), 53(17), 39(37), and 27(16).

(4) trans-1-*Chlorocyanomethyl*-2-*trifluoromethylcyclopropane*. Reductions were carried out under a variety of conditions (see Table 1).

At room temperature the reaction in the absence of a solvent took place quantitatively, but at −25 °C, the extent of reduction was limited to 90%, and in heptane (see Table 1) the yield was 50%. The products were analysed by g.l.c., in comparison with the authentic compounds (see above). (SiDC 550 15% on Chromosorb W 80—100; 3 mm × 3 m; N_2 at 20 cm^3 min^{-1}; 100 °C). Under these conditions, the order of elution is *trans*-$CF_3CH_2CH_2CH{=}CHCN$, 1-cyanomethyl-2-trifluoromethylcyclopropane, 1-chlorocyanomethyl-2-trifluoromethylcyclopropane, *cis*-$CF_3CH_2CH_2CH{=}CHCN$; *m/e* (*trans*-$CF_3CH_2CH_2CH{=}CHCN$) 149(66%), 129(27), 122(66), 109(27), 102(100), 80(62), 77(20), 69(21), 66(86), 65(30), 64(39), 54(26), 53(89), 52(27), 51(30), 41(21), 39(67), and 27(39); *cis*-$CF_3CH_2CH_2CH{=}CHCN$ 149(65%), 129(33), 122(60), 109(29), 102(89), 80(47), 77(21), 69(20), 66(100), 64(37), 54(21), 53(72), 52(22), 51(26), 41(26), 39(58), and 27(32).

E.s.r. Experiments.—A mixture of the cyclopropyl compound, di-t-butyl peroxide, and cyclopropane solvent, in the ratio 1:1:5 by volume, was sealed in Suprasil silica tubes, and photolysed with light from a Philips SP 500 mercury arc in the cavity of a Varian E4 spectrometer, by the procedure described previously.[8]

Acknowledgements

We acknowledge support from NATO, the S.E.R.C., and the Central Research Fund of the University of London.

References

1 J.-Y. Godet and M. Pereyre, *Tetrahedron Lett.*, 1970, 3653.
2 J.-Y. Godet and M. Pereyre, *Compt. rend.* (*C*), 1971, **273**, 1183.
3 J.-Y. Godet and M. Pereyre, *J. Organomet. Chem.*, 1972, **40**, C23.
4 J.-Y. Godet and M. Pereyre, *Compt. rend. C*, 1973, **277**, 211.
5 J.-Y. Godet, M. Pereyre, J.-C. Pommier, and D. Chevolleau, *J. Organomet. Chem.*, 1973, **55**, C15.
6 A. G. Davies, J.-Y. Godet, B. Muggleton, and M. Pereyre, *J. Chem. Soc., Chem. Commun.*, 1976, 813.
7 P. M. Blum, A. G. Davies, M. Pereyre, and M. Ratier, *J. Chem. Soc., Chem. Commun.*, 1976, 814.
8 A. G. Davies, B. Muggleton, J.-Y. Godet, M. Pereyre, and J.-C. Pommier, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1719.
9 M. Castaing, M. Pereyre, M. Ratier, P. M. Blum, and A. G. Davies, *J. Chem. Soc., Perkin Trans. 2*, 1979, 287.
10 M. Castaing, M. Pereyre, M. Ratier, P. M. Blum, and A. G. Davies, *J. Chem. Soc., Perkin Trans. 2*, 1979, 589.
11 P. M. Blum, A. G. Davies, M. Pereyre, and M. Ratier, *J. Chem. Res.*, (*S*) 1980, 110; (*M*) 1980, 1174.
12 P. S. Mariano and E. Bay, *J. Org. Chem.*, 1980, **45**, 1763.
13 M. C. Böhm, K. D. Sen, and P. C. Schmidt, *Chem. Phys. Lett.*, 1981, **78**, 357.
14 I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley, New York, 1976.
15 M. Hanack and H. Meyer, *Justus Liebigs Ann. Chem.*, 1968, **720**, 81.
16 P. A. Wehrli and V. Chu, *J. Org. Chem.*, 1973, **38**, 3436.
17 P. Brown, J. Burdon, T. J. Smith, and T. C. Tatlow, *Tetrahedron*, 1960, **10**, 164.
18 L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon Press, Oxford, 2nd edn., 1969; T. Shono, T. Morikawa, A. Oku, and R. Oda, *Tetrahedron Lett.*, 1964, 791.
19 E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 1975, 2647.

20 *Cf.* V. Migrdichian, 'Organic Synthesis,' Reinhold, New York, 1957, vol. 1, p. 145.
21 *Cf.* M. E. Herr and F. W. Heyl, *J. Am. Chem. Soc.*, 1950, **72**, 1753.
22 *Cf.* B. A. Pawson, H. C. Cheung, S. Gurbaxani, and G. Saucy, *J. Am. Chem. Soc.*, 1970, **92**, 336.
23 A. L. Henne, M. S. Newman, L. L. Quill, and R. A. Staniforth, *J. Am. Chem. Soc.*, 1947, **69**, 1819.
24 G. F. Grillot, S. Aftergut, S. Marmor, and F. Carrock, *J. Org. Chem.*, 1958, **23**, 386.
25 E. T. McBee, O. R. Pierce, and D. D. Smith, *J. Am. Chem. Soc.*, 1954, **76**, 3722.
26 *Cf.* K. L. Erickson, J. Markstein, and K. Kim, *J. Org. Chem.*, 1971, **36**, 1024.

Received 20*th February* 1984; *Paper* 4/293