# Regioselectivity in the Ring-opening of 2-Methylcyclopropylcarbinyl and 2-Methylcyclobutylcarbinyl Radicals

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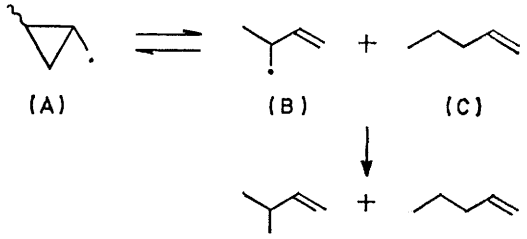
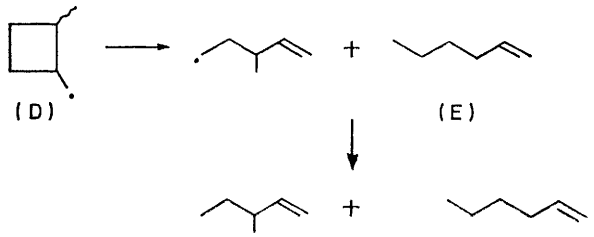
The methylcyclopropylcarbinyl radical *trans*-(A) was generated by treating the corresponding chloride or bromide with tributyltin hydride at 25 and 45 °C, and the regioselectivity of ring-opening was determined by g.l.c. analysis of the alkenes which were formed. The intermediate radical (B) was also prepared from the corresponding acyclic bromide.




It is shown that the ring-opening is regioselective in favour of the primary alkyl radical (B) but that, when the concentration of tin hydride is low, the acyclic radicals (B) and (C) can equilibrate through the cyclic radical (A).

The radicals, *cis*- and *trans*-(A), and (B) and (C), were also generated photolytically at low temperature, and were monitored by e.s.r. spectroscopy. Ring-opening of (A) is now irreversible, and whereas *cis*-(A) gives principally the secondary alkyl radical (C), the *trans*-(A) compounds again give principally the primary alkyl radicals (B).

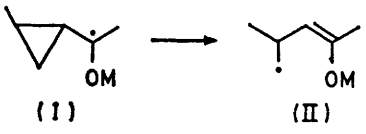
The *cis*- and *trans*-2-methylcyclobutylcarbinyl radicals (D) were generated by treating the corresponding chloride and bromide with tributyltin hydride, and again the course of the reaction was determined by g.l.c. analysis of the products.




Ring opening is now relatively slow and irreversible, and both *cis*- and *trans*-(D) give principally the secondary alkyl radical (E).

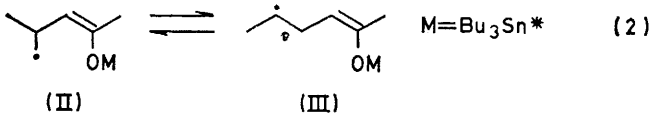
We have recently studied the ring opening of 2-methyl substituted cyclopropyl(stannyloxy)carbinyl and (hydroxy)carbinyl radicals, by means of product analysis and e.s.r. spectroscopy.[1,2]

The main feature found is that, under kinetic control, *trans*-radicals (I) give in major amount the primary, thermodynamically less-stable, ring-opened radicals (II).




However, we noticed that under suitable conditions the first-formed primary radical can undergo equilibration to the more stable secondary one (III) [equation (2)].[2]

We wish to report here complementary and comparative studies which we have performed on 2-methylcyclopropylcarbinyl [3] and 2-methylcyclobutylcarbinyl free radicals, both obtained from the corresponding halides.



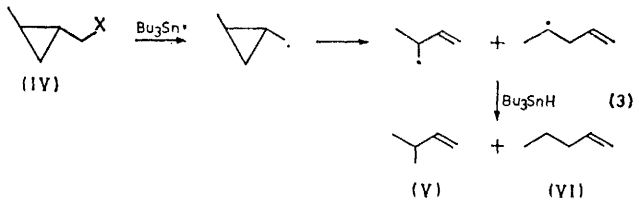

* When M = H, the *cis*-4-hydroxybut-3-enyl radicals (II) and (III) undergo rapid 1,5-hydrogen transfer to give buten-1-oxyl radicals.

*Ring-opening of 2-Methylcyclopropylcarbinyl Radicals.*—*trans*-2-Methylcyclopropylcarbinyl halides (IV) were caused to react, under free-radical conditions, with tributyltin hydride, and the ring-opened radicals were monitored as the corresponding olefins (V) and (VI) by g.l.c.

The results of experiments under different experimental conditions are gathered in Table 1.

Only 3-methylbut-1-ene (V) and pent-1-ene (VI) were

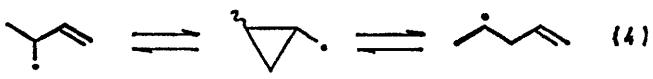
obtained [equation (3)], and no dimethylcyclopropane was detected. Under suitable conditions, 3-methylbut-1-ene (V), derived from the primary alkyl radical is the major product, but the regioselectivity of the reaction



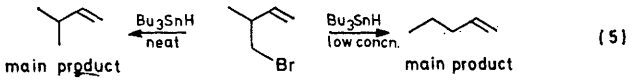

depends on the nature of the halide used (chloride or bromide), on the reaction temperature, and particularly on the tin hydride concentration.

The highest yield of 3-methylbut-1-ene, arising from the primary radical, is obtained from reactions between the neat reagents. The data show again that the first-formed radical is the less stable one, which is trapped more easily at the highest concentration of reducing agent. The selectivity of ring opening apparently increases as the temperature is reduced (from 45 to 25 °C) and this is confirmed by the e.s.r. experiments at much lower temperatures which are reported below.

On dilution, the reduction tends to give mainly pent-1-ene arising from the more stable radical. We assume that, under these conditions, the hydrogen-transfer step is slow enough to allow equilibration of radicals through ring re-closing and re-opening.[4]


(4)

This has been confirmed by studying the tin hydride reductions of the 4-bromo-3-methylbut-1-ene under the same conditions, when the reaction was found to follow a different course depending on the concentration of tin hydride:



(5)

The results are shown in Table 2. Rearrangements of the same kind, though less extensive, have already been reported for similar reductions of 3-(bromomethyl)-cyclopentene and 4-chlorocycloheptene.[5]

TABLE 1

Percentage yields of alkenes from the reduction of *trans*-2-methylcyclopropylcarbinyl halides with tributyltin hydride

| | | Experimental conditions [c] | | | |
|---|---|---|---|---|---|
| | Olefins [a,b] | 25 °C neat | 45 °C neat | 45 °C 0.2M in PhH | 45 °C 0.02M in PhH |
| X = Br |  | 66.1 | 52.8 | 25.9 | 8.2 |
| |  | 33.9 | 47.2 | 74.1 | 91.8 |
| X = Cl |  | 58.7 | 46.9 | 22.2 | 3.5 |
| |  | 41.3 | 53.1 | 77.8 | 96.5 |

[a] Overall reduction yields were *ca.* 85% in each case except with the chloride in dilute solution (*ca.* 60%). [b] It was confirmed in separate experiments that reduction of the alkenes by the tin hydrides was not significant under the conditions of the reactions. [c] Equimolecular amounts of reagents. Experiments at 45 °C initiated with azobisisobutyronitrile (AIBN) and at 25 °C with u.v. light through Pyrex.

TABLE 2

Percentage yields of alkenes from the reduction of 4-bromo-3-methylbut-1-ene with tributyltin hydride

| | Experimental conditions [b] | | |
|---|---|---|---|
| Olefins [a] | 45 °C neat | 45 °C 0.2M in PhH | 45 °C 0.02M in PhH |
|  | 90 | 41 | 14 (8) |
|  | 10 | 59 | 86 (92) |

[a] Overall reduction yields were *ca.* 85%. [b] Equimolar amounts of reagents; experiments were run in the presence of AIBN except the results in parenthesis which were obtained under u.v. irradiation through Pyrex.

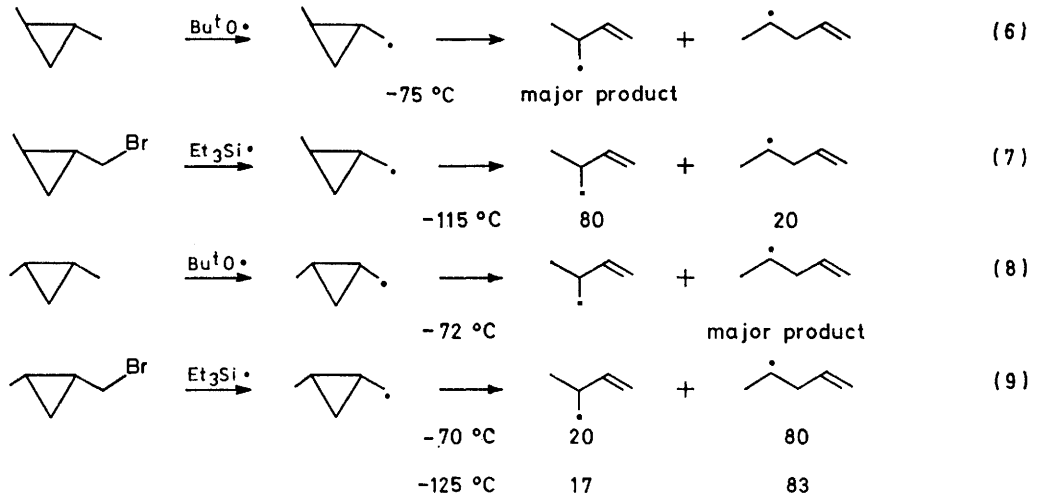
The final point to be drawn from the data in Table 1 is the comparison between the products obtained from reduction of the bromide and of the chloride. Under the same conditions, the two halides show regioselectivities which are similar but not identical. This is surprising at first sight, since the cyclopropylcarbinyl radicals once they are formed from either source should be indistinguishable and not betray their origins.

Some years ago, different extents of rearrangements in the tin hydride reduction of γ-silyl bromides and chlorides were reported and interpreted as arising from the halogen abstraction step by the tin radical: bromide was abstracted normally while abstraction of chlorine was assisted by participation of one phenyl group bound to silicon.[6] We prefer here to account for the small differences observed between the chloride and bromide on the basis that the reduction of bromides, often exothermic, is much easier than the reduction of chlorides.[7]

The reaction of the bromides has probably already taken place to some extent in the period between the preparation of the mixture of reagents (at lower temperature) and the beginning of heating (or irradiating) the mixture. Since the ratio of 3-methylbut-1-ene to pent-1-ene depends on a number of factors (regioselectivity of ring-opening, equilibrium constants, rate constants for hydrogen transfer), and increases at lower temperatures, the reduction of the bromides might be expected to give the higher ratio of 3-methylbut-1-ene, as is observed. Similar considerations may be relevant to the results reported in ref. 6.

A parallel series of reactions [equations (6)—(9)] was carried out in which the 2-methylcyclopropylcarbinyl

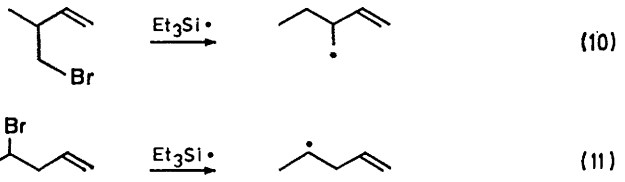
radicals shown were generated photolytically in cyclopropane solution in the cavity of an e.s.r. spectrometer.[3] The relative concentrations of the radicals which were observed at various temperatures are recorded under the appropriate formulae.




Only the radicals resulting from ring-opening were observed, and in no case could the parent cyclopropylcarbinyl radical be detected, even at −140 °C. In contrast, the unsubstituted cyclopropylmethyl radical can be detected at −120 °C;[8] apparently the introduction of a *cis*- or *trans*-2-methyl group enhances the rate of ring opening.

In reactions (6) and (8), the spectra were weak; the spectrum of the radical noted as the major product could be distinguished, but that of the minor product was below the noise level of the instrument. Reactions (7) and (9) afforded much stronger spectra, and the relative concentrations of the two radicals could be measured. Consistently, however, it is observed that the *trans*-2-methylcyclopropylcarbinyl radical undergoes ring-opening to give preferentially the primary alkyl radical.

The 1-methyl- and 2-methyl-but-3-enyl radicals were



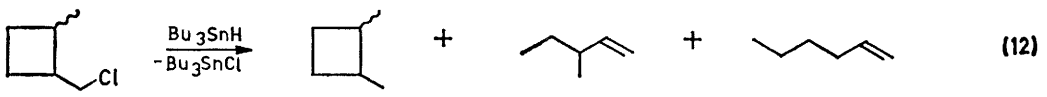

also generated by treating the appropriate bromides with triethylsilyl radicals [equations (10) and (11)].

In each case, the only spectrum which was observed over the temperature range −20 to −100 °C was that of the radical with the structure corresponding to that of the parent bromide. This confirms that the equilibration of equation (4) does not occur to a detectable degree under the conditions of the e.s.r. experiment.

These experiments at low temperatures by the e.s.r. technique where the radical intermediates are monitored under conditions of complete kinetic control endorse and extend those at higher temperatures where the reaction products are analysed and the conditions can be varied to demonstrate the preponderance of either thermodynamic control or of kinetic control of products. Together, they establish that the remarkable effect of a *trans*-2-methyl substituent in inducing the formation of a primary rather than a secondary ring-opened alkyl radical is not confined to the cyclopropylcarbinols and their organotin derivatives [equation (1)],[1] but is apparently general for other cyclopropyl compounds.[3] We hope to return to the question of the origin of this effect in a subsequent paper.

*Ring-opening of 2-Methylcyclobutylcarbinyl Radicals.*—The reduction of *cis*- and *trans*-2-methylcyclobutylcarbinyl chlorides with tributyltin hydride in 0.02M-concentration in benzene at 80 °C, was described recently by Hill and his co-workers.[9] The percentage yields of products are given in equation (12).

These data show that the ring opening of both *cis*- and *trans*-2-methylcyclobutylcarbinyl radicals yields mainly the secondary, more stable, radical. Since we have shown above that the ring-opening of the corresponding 2-methylcyclopropylcarbinyl radicals is under thermodynamic control at this concentration of tributyltin hydride, we wondered whether the result obtained with the *trans*-chloride could be reversed under different conditions.



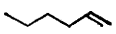
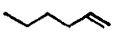

| | | | |
|---|---|---|---|
| *cis* | 16 | 1.5 | 82.5 |
| *trans* | ⩾36 | ⩽5 | 59 |

*cis*- and *trans*-2-Methylcyclobutylcarbinyl chloride were reduced with tributyltin hydride, and the products were analysed by g.l.c. The reaction conditions, and

the relative yields of products, are shown in Table 3.

TABLE 3

Percentage yields of products from the reduction of 2-methylcyclobutylcarbinyl chlorides with tributyltin hydride

| | Products [a] | Experimental conditions [b] 100 °C neat | 80 °C neat | 80 °C 0.2M in PhH | 80 °C 0.02M in PhH |
|---|---|---|---|---|---|
| |  | 65 | 79.2 | 55.2 | 15.3 |
| *trans* |  | 4.9 | 2.7 | 5 | 8.3 |
| |  | 30.1 | 18 | 39.8 | 76.4 |
| |  | 53.6 | 79.8 | 31 | 9.3 |
| *cis* |  | 1.3 | 0.6 | 1.6 | 1.7 |
| |  | 45.1 | 19.6 | 67.4 | 89 |

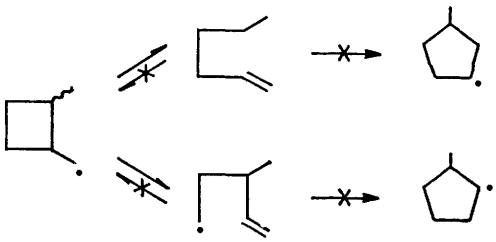
[a] Overall reduction yields were *ca.* 85% except with chlorides in dilute solution (*ca.* 60%). [b] Equimolecular amounts of reagents. Initiation with AIBN.

Three significant points emerge.

First, as expected, cyclobutylcarbinyl radicals rearrange more slowly than cyclopropyl ones.[10,11] The amount of ring-opening increases at higher dilution or higher temperature. Under the former conditions, the first-formed cyclobutylcarbinyl radical reacts slowly with the tin hydride and is given the opportunity for more extensive unimolecular rearrangement. If cyclobutylcarbinyl radicals are generated photolytically in the cavity of an e.s.r. spectrometer at low temperature, the spectra of only these radicals, and none of those which would result from ring-opening, are observed.[12]

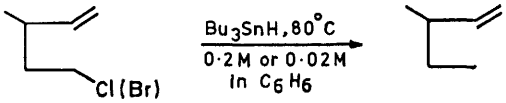
Second, even under the most favourable conditions for kinetic control (neat reagents), both *cis*- and *trans*-isomers give mainly hex-1-ene arising from the secondary radical. However, it is interesting to note that the 3-methylpent-1-ene/hex-1-ene ratio, as observed by Hill,[9] is usually higher from the *trans*-chloride. Similar results have recently been obtained by Beckwith and Moad.[13]

Third, in both cases there is apparently a slight shift of the above ratios towards hex-1-ene with increasing dilution. However, the reduction of the *cis*-chloride gave no significant amounts of *trans*-dimethylcyclobutane. Moreover, no methylcyclopentane, arising from an hypothetical reclosing of the opened radical,[14] was formed even at the highest dilution. This point, difficult to establish since even carefully purified benzene contains small amounts of methylcyclopentane, was confirmed by experiments we conducted in decalin solution, as well as by Beckwith's data.[13] It appears thus that no free radical re-closing and re-opening occurs [equation (13)], and that even at 0.02M-concentration the reactions are mainly under kinetic control.



(13)

To confirm this, we carried out a series of reductions on the isomeric acyclic halides [equations (14) and (15)], and whatever the conditions, obtained only the normal, non-rearranged olefin.

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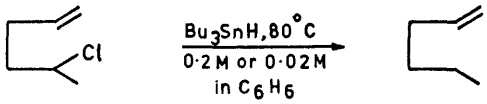


(15)

Some experiments were also carried out with the *cis*- and *trans*-2-methylcyclobutylcarbinyl bromides. Using the same experimental conditions as for the corresponding chlorides we obtained similar results but with higher amounts of dimethylcyclobutane. Here again, the reductions probably start as soon as the reagents are mixed at 0 °C, and before the reaction mixtures reach the temperature of the experiment.

*Conclusion.*—In summary, 2-methylcyclopropylcarbinyl and 2-methylcyclobutylcarbinyl free radicals show the following differences in behaviour.

First, both undergo ring-opening, but that of the cyclobutyl compounds is relatively slow.

Secondly, under kinetic control, the *trans*-2-methylcyclopropylcarbinyl radicals tend to give mainly the thermodynamically less-stable ring-opened radicals, but the more stable radicals are obtained from the cyclobutylcarbinyl radicals.

Thirdly, conditions for thermodynamic control are easily reached with the cyclopropylcarbinyl compounds, but no such equilibration occurs with cyclobutylcarbinyl radicals.

## EXPERIMENTAL

*Techniques.*—N.m.r. spectra were recorded on a Perkin-Elmer R12 (60 MHz) or Varian HA100 (100 MHz) spectrometer, with tetramethylsilane as internal standard. Preparative g.l.c. was carried out on an Aerograph Autoprep A700 or Varian 712 chromatograph, and analytical g.l.c. on an Intersmat IGC 120 FB or Perkin-Elmer F11 instrument, both with flame ionisation detection.

E.s.r. spectra were recorded on a Varian E4 spectrometer fitted with a Philips SP 500 or CS/500 high-pressure mercury-arc lamp and quartz optical system for photolysis in the

cavity. Samples in cyclopropane solvent were sealed under vacuum in Suprasil silica tubes.[1]

t-Butoxyl radicals were derived from the photolysis of di-t-butyl peroxide, and triethylsilyl radicals from di-t-butyl peroxide and triethylsilane.

To determine the ratio of primary to secondary alkyl radicals resulting from ring-opening reactions, the spectrum of each was simulated by computer using the hyperfine coupling constants determined for the radicals derived from the acyclic bromides. The two spectra were superimposed and their relative intensities were varied to give the best fit with the observed spectrum.

The hyperfine coupling constants of the radicals in cyclopropane at −75 °C were as follows:

$CH_2$=$CHCH(CH_3)CH_2$•, $a$(2Hα) 21.9, $a$(Hβ) 29.0 G
$CH_2$=$CHCH_2\dot{C}HCH_3$, $a$(Hα) 21.0, $a$(5Hβ) 23.6 G

## *Materials*

*Tributyltin Hydride.*—This compound was prepared by reducing bis(tributyltin) oxide (Rhône-Poulenc) with polymethylsiloxane (Rhône-Poulenc);[15] b.p. 80—82 °C at 0.7 mmHg; 88% yield.

cis-1,2-*Dimethylcyclopropane.*[16]—*cis*-But-2-ene was treated with bromoform in the presence of potassium t-butoxide to give 1,1-dibromo-*cis*-2,3-dimethylcyclopropane, b.p. 67—70 °C at 20 mmHg, in 75% yield; δ($C_6H_6$) 0.84 (2 H, b, C*H*$CH_3$) and 1.13 (6 H, b, $CH_3$). This was then reduced with polymethylsiloxane in the presence of bis(tributyltin) oxide to give *cis*-1,2-dimethylcyclopropane which was collected in a trap at −80 °C and 20 mmHg, and then purified by preparative g.l.c. (silicone oil at room temperature); δ($C_6H_6$) 0.27 (2 H, s, $CH_2$), 0.64 (2 H, b, C*H*$CH_3$), and 1.0 (6 H, d, $CH_3$; $J$ 4.5 Hz).

trans-1,2-*Dimethylcyclopropane.*—By a similar procedure, 1,1-dibromo-*trans*-2,3-dimethylcyclopropane, b.p. 60—66 °C at 20 mmHg (80% yield), δ($C_6H_6$) 0.9 (2 H, s, C*H*$CH_3$) and 1.14 (6 H, s, $CH_3$) was first prepared from *trans*-but-2-ene. This was then reduced to *trans*-1,2-dimethylcyclopropane, δ($C_6H_6$) 0.78 (2 H, b, $CH_2$), 1.07 (2 H, s, C*H*$CH_3$), and 1.16 (6 H, s, $CH_3$).

trans-2-*Methylcyclopropylcarbinyl Halides.*—*trans*-2-Methylcyclopropylcarbinol was prepared from crotyl alcohol, itself obtained by lithium aluminium hydride reductive of *trans*-crotonaldehyde,[17] by means of Simmons–Smith cyclopropanation according to a published procedure.[18] Its characteristics agreed with those in the literature:[19] b.p. 60 °C at 30 mmHg, δ($CCl_4$) 0.2—0.8 (4 H, b, ring), 1.04 (3 H, d, $CH_3$), and 3.31 (2 H, d, $CH_2$).

trans-2-*Methylcyclopropylcarbinyl bromide.* This compound was obtained by reaction of the carbinol with $PBr_3$–pyridine according to a general procedure.[20] The n.m.r. spectrum of the product (49% yield, b.p. 58—60 °C at 80 mmHg) showed signals due to olefinic contaminants which were removed by preparative g.l.c. (30% Castorwax on Chromosorb W60–100, $t$ 60 °C, helium at 150 ml $min^{-1}$); δ($CCl_4$) 0.4—0.9 (4 H, b, ring), 1.07 (3 H, d, $CH_3$), and 3.22 (2 H, d, $CH_2$).

trans-2-*Methylcyclopropylcarbinyl chloride.* This compound was obtained by treating the carbinol with thionyl chloride and pyridine by a general method.[21] The n.m.r. spectrum of the product (40% yield, b.p. 48—50 °C at 80 mmHg) revealed impurities which were removed by preparative g.l.c. (30% Castorwax on Chromosorb W60–100, $t$ 50 °C, helium); δ($CCl_4$) 0.3—0.9 (4 H, b, ring), 1.08 (3 H, d, $CH_3$), and 3.30 (2 H, d, $CH_2$).

cis- *and* trans-2-*Methylcyclopropylcarbinyl bromides.* These compounds were also obtained by preparing trimethyl-1-(methylbut-3-enyl)tin from 1-methylbut-3-enylmagnesium bromide and tributyltin chloride, then treating the crude product with bromine at −78 °C. The mixture was allowed to come to room temperature over 1 h, and then the products were collected at 1 mmHg, and purified by preparative g.l.c.; *trans*-isomer, δ($C_6H_6$) 0.15—1.04 (ring $CHCH_2CH$), 0.82 (d, $CH_3CH$; $J$ 6 Hz), and 2.90 (d, $BrCH_2$; $J$ 7 Hz); *cis*-isomer, δ($C_6H_6$) 0.35—1.15 (ring $CHCH_2CH$), 0.85 (b, $CH_3$), and 2.8—3.3 (m, $CH_2Br$).

2-*Methylcyclobutylcarbinyl Halides.*—A mixture of *cis*- and *trans*-2-methylcyclobutylcarbinol was obtained [9] by preparing 2-methylcyclobutanecarboxylic acid,[19,22] which was then reduced with lithium aluminium hydride.[23]

2-*Methylcyclobutylcarbinyl chlorides.* These compounds were obtained from the alcohols by reaction with $SOCl_2$ in the presence of tri-n-butylamine.[9] The mixed isomers (58% *trans*, 42% *cis*), b.p. 124 °C, 32% yield, were separated by preparative g.l.c. (20% Castorwax 20M on Chromosorb W60–80, $t$ 70 °C, helium 200 ml $min^{-1}$); the n.m.r. spectra were in agreement with the literature:[9] *trans* δ($CCl_4$) 1.10 (3 H, d, $CH_3$), 1.54 (2 H, b, ring), 2.07 (4 H, b, ring), and 3.44 (2 H, d, $CH_2$); *cis* δ($CCl_4$) 1.06 (3 H, d, $CH_3$), 1.65 (2 H, b, ring), 2.05 (2 H, b, ring), 2.60 (2 H, b, ring), and 3.45 (2 H, b, $CH_2$).

2-*Methylcyclobutylcarbinyl bromides.* These compounds were obtained by treating the alcohols with phosphorus tribromide and pyridine as for the cyclopropyl compounds. The product (b.p. 137 °C, 49% yield) consisted mainly of the two isomeric cyclobutyl bromides together with some cyclopentyl bromide, which were separated under the same conditions of preparative g.l.c. as those used for the corresponding chlorides: *trans* δ($CCl_4$) 1.08 (3 H, d, $CH_3$), 1.52 (2 H, b, ring), 2.04 (4 H, b, ring), and 3.28 (2 H, d, $CH_2$); *cis* δ($CCl_4$) 1.05 (3 H, d, $CH_3$), 1.63 (2 H, b, ring), 1.97 (2 H, b, ring), 2.50 (2 H, b, ring), and 3.33 (2 H, d, $CH_2$).

*Acyclic Alkenyl Halides.*—4-*Bromopent*-1-*ene.* Phosphorus tribromide (49 g) was added dropwise during 4 h to a well-stirred mixture of 4-methylbut-1-en-4-ol (43 g) and pyridine (10 g) at −30 °C. The mixture was then heated on a water-bath for 1 h and finally worked up to yield the bromide, b.p. 60—65 °C at 90 mmHg; δ (in $C_6H_6$) 1.37 (3 H, d, $CH_3$), 2.29 (2 H, d. $CH_2$; $J$ 7.2 Hz), 3.72 (1 H, sextet, CHBr), 4.82 (1 H, b, =CH−), 5.07 [1 H, b, =C(*H*)H], and 5.5 [1 H, b, =C(H)*H*].

4-*Bromo*-3-*methylbut*-1-*ene.* This compound was prepared by the reaction of $PBr_3$–pyridine on the corresponding alcohol which itself was obtained by the reaction of crotylmagnesium chloride with formaldehyde. The n.m.r. spectrum of the product (b.p. 75 °C at 200 mmHg, 40% yield) was in accord with its structure: δ($CCl_4$) 1.13 (3 H, d, $CH_3$), 2.55 (1 H, b, H), 3.26 (2 H, 2d, $CH_2$), and 4.84—6.02 (3 H, b, $CH{:}CH_2$).

5-*Chloro*-3-*methylpent*-1-*ene.* This compound was prepared by the reaction of $SOCl_2$ and pyridine on the corresponding alcohol, itself obtained by the reaction of crotylmagnesium chloride with ethylene oxide. The product (b.p. 103 °C, 34% yield) showed n.m.r. characteristics in agreement with its structure: δ($CCl_4$) 1.02 (3 H, d, $CH_3$), 1.71 (2 H, q, $CH_2$), 2.38 (1 H, b, H), 3.42 (2 H, t, $CH_2$), and 4.75—5.84 (3 H, b, $CH{:}CH_2$).

5-*Bromo*-3-*methylpent*-1-*ene.* This compound was ob-

tained from the alcohol by the $PBr_3$–pyridine procedure. The product (b.p. 52—54 °C at 40 mmHg, 46% yield) had a satisfactory n.m.r. spectrum: δ($CCl_4$) 1.01 (3 H, d, $CH_3$), 1.8 (2 H, q, $CH_2$), 2.35 (1 H, b, H), 3.26 (2 H, t, $CH_2$), and 4.73—5.77 (3 H, b, $CH{=}CH_2$).

*5-Chlorohex-1-ene.* This compound was obtained from the corresponding alcohol, itself prepared by reduction of hex-5-en-2-one with lithium aluminium hydride.[24] The product (b.p. 65 °C at 130 mmHg, 46% yield) showed δ($CCl_4$) 1.42 (3 H, d, $CH_3$), 1.64—1.84 (2 H, b, $CH_2$), 1.87—2.3 (2 H, b, allylic $CH_2$), 3.84 (1 H, b, H), and 4.7—5.95 (3 H, b, $CH{:}CH_2$).

*Reactions of Halides with Tributyltin Hydride.*—Equimolecular amounts of reagents were used in each case. Benzene was distilled and kept on sodium wire. The solutions were prepared at room temperature for the chlorides and at 0 °C for the bromides by the following general method: the halides were weighed and dissolved in a major part of the necessary solvent, then were added successively the equivalent amount of tin hydride, the complement of solvent to reach the desired concentration, and about 5% (w/w) of azobisisobutyronitrile (except for experiments to be run under u.v. light). A part of the solution (2—3 ml) was then transferred to a small Pyrex tube which was sealed under argon and heated in a thermostatted bath (or in one case irradiated by the light from a Philips HPK 125 bulb). Reagent mixtures without solvent were also prepared at 0 °C for the bromides or room temperature for chlorides, and the tubes sealed under argon.

Heating (or irradiation) was continued for approximately 44 h (solution) or 16 h (neat). The tubes were cooled and opened and the composition of the products and the overall reduction yields (usually 80—90%, except for the chlorides in dilute solution, which were about 60%) were determined by g.l.c.

The product compositions given in the Tables are the averages of several g.l.c. analyses of the same samples. In some cases experiments were duplicated and gave very similar data.

3-Methylbut-1-ene and pent-1-ene were identified and quantitatively determined by comparison by g.l.c. with samples which were authenticated by n.m.r. (10% UCON 50 HB 2000 on Chromosorb XY + 15% XF 1150 on Chromosorb P, *t* 30 °C).

The reduction products of 2-methylcyclobutylcarbinyl halides were identified and quantitatively determined by comparison with authentic samples (15% SI DC 550 on Chromosorb W, *t* 30 °C).

Reference samples of 3-methylpent-1-ene and hex-1-ene came from preparative-scale reduction of 5-chloro-3-methylpent-1-ene and 5-chlorohex-1-ene with tributyltin hydride and AIBN at 80 °C without solvent. 3-Methylpent-1-ene (81% yield, b.p. 54 °C), δ($CCl_4$) 0.88 (3 H, d, $CH_3$), 0.96—1.33 (5 H, b, $CH_2CH_3$), 1.97 (1 H, b, H), 4.68—5.88 (3 H, b, $CH{=}CH_2$). Hex-1-ene (78% yield, b.p. 63 °C), δ($CCl_4$) 0.86 (3 H, t, $CH_3$), 1.8 (4 H, m, $CH_2$), 2.04 (2 H, m, allylic $CH_2$), and 4.8—6.18 (3 H, b, $CH{=}CH_2$).

Reference samples of *cis*- and *trans*-1,2-dimethylcyclobutane were obtained from the mixture of *cis*- and *trans*-2-methylcyclobutylcarbinols by converting them into the tosylates which were reduced with lithium aluminium hydride. The *trans*-isomer had a shorter retention time than the *cis*-isomer.

We detected the presence of minute amounts of *trans*-1,2-dimethylcyclobutane in the products of experiments performed with the *cis*-chloride, but this was attributed to small amounts of *trans*-chloride still contaminating the *cis*-isomer after the preparative g.l.c. separation. The absence of methylcyclopentane was difficult to establish since benzene contained a small amount of this material and of cyclohexane, but the equality of the ratio methylcyclopentane : cyclohexane in the starting solvent and in the reaction products showed that no more than negligible amounts of methylcyclopentane are formed even under the conditions of lowest concentration. This was confirmed by carrying out the same reactions in decalin as solvent.

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