Ring-opening of Some Radicals containing the Cyclopropylmethyl System

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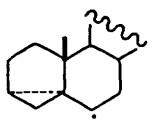
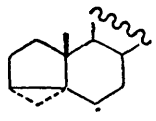
Mono- and bi-cyclic radicals containing the cyclopropylmethyl system are readily generated by interaction of the appropriate halides with triphenyl- or tributyl-stannane. Each radical studied underwent ring-opening by fission of the more substituted βγ-bond. In the case of the secondary radical (12b) the new double bond was formed preferentially in the *trans*-configuration. Rate constants, which cannot be determined with high accuracy by this method, lie in the range 1×10^7—3×10^8 s^{-1} at 25 °C. When generated by the flow method in the e.s.r. cavity α-hydroxycyclopropylmethyl radicals undergo β-fission followed by 1,5-hydrogen atom transfer to afford enoxyl radicals. The latter reaction occurs more slowly in water than in non-polar solvents. The rigid hydroxynortricyclyl radical (43) undergoes preferential fission of the less substituted βγ-bond, possibly because of the dipolar nature of the transition state.

DESPITE the importance of the cyclopropylmethyl–allylmethyl radical rearrangement as a mechanistic probe and kinetic standard,[1] relatively little is known about the rates of rearrangement of substituted systems. An e.s.r. method has been employed [2] to determine the activation parameters and rate constant (k_f 1.3×10^8 s^{-1} at 25 °C) for ring-opening of the parent cyclopropylmethyl radical. An earlier estimate [3] gave a lower limit of k_f of 3×10^7 s^{-1} at 80 °C whilst a value (k_f *ca.* 6×10^7 s^{-1}) of somewhat doubtful accuracy (see below) can be obtained by the usual treatment [4] of data recently reported [5] for the reaction of cyclopropylmethyl bromide with tributylstannane. Application of the tin hydride method [4] to suitable halo geno-compounds has similarly afforded values of the rate constants for β-fission of the nortricyclyl radical (k_f *ca.* 1×10^8 s^{-1} at 45 °C) [4] and of the isomeric steroid radicals (1) and (2) (k_f *ca.* 4×10^7 at 25 °C in each case).[6] The direction of ring opening of radicals (1) and (2) and similar rigid species [7] indicates that β-fission of cyclopropylmethyl radicals is under stereoelectronic control [8] and proceeds by fission of that bond which is most nearly in the eclipsed orientation with respect to the semi-occupied orbital.

cis-2-Methylcyclopropylmethyl radical (3) [9,10] and related α-oxygenated species (4) [10,11] undergo rearrangement to afford mainly the thermodynamically favoured secondary alkyl radicals (7) and (8). Unexpectedly, their *trans*-isomers (5) and (6) give mainly the less stable primary radicals (9) and (10) under conditions favouring kinetic control, although equilibration to afford the secondary radicals can occur under suitable experimental conditions.[9-11] Equally unexpected is the conclusion that may be drawn from recent e.s.r. and kinetic data [5,9] that rearrangement of *trans*-2-methylcyclopropylmethyl radical (5) to the primary radical (9) proceeds *more rapidly* than rearrangement of the parent radical (12a). No completely satisfactory explanation for the anomalous behaviour of the *trans*-2-methylcyclopropylmethyl system has yet been advanced. It has been suggested [10,11] that polar or conformational factors may be important, but the validity of these hypotheses cannot be tested until further kinetic data are available. The present work was undertaken with the aims of examining the utility of the stannane method for obtaining such data, of exploring the applications of the e.s.r. flow system in this area, and of investigating the importance of polar and conformational effects on the rearrangement of a rigid cyclopropylmethyl radical.

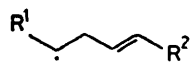


(1)

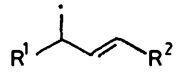


(2)

(3) R^1 = *cis*-Me, R^2 = H
(4) R^1 = *cis*-Me, R^2 = OH or $OSnBu_3$
(5) R^1 = *trans*-Me, R^2 = H
(6) R^1 = *trans*-Me, R^2 = OH or $OSnBu_3$



(7) R^1 = Me, R^2 = H
(8) R^1 = Me, R^2 = OH or $OSnBu_3$

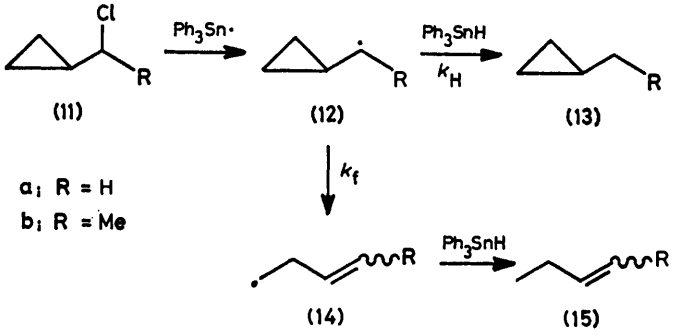


(9) R^1 = Me, R^2 = H
(10) R^1 = Me, R^2 = OH or $OSnBu_3$

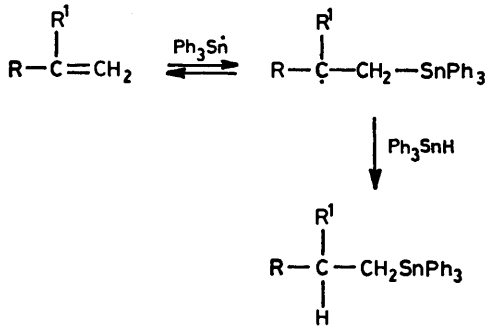
Reactions of Triphenylstannane with Cyclopropylmethyl Chlorides.—Previous work has shown that the rate of hydrogen-atom transfer from tributylstannane to cyclopropylmethyl and related radicals is marginally too slow to allow rearrangement rates to be accurately determined. For example, the reaction of cyclopropylmethyl bromide with neat tributylstannane (3.8M) affords only 8% of methylcyclopropane,[5] whilst *trans*-2-

methylcyclopropylmethyl halides under similar conditions give solely ring-opened products.[9]

Triphenylstannane undergoes hydrogen-atom transfer to alkyl radicals more rapidly than does tributylstannane [4] and it should, therefore, be a more effective reagent for trapping cyclopropylmethyl radicals before they undergo rearrangement. However, when cyclopropylmethyl chloride (11a) was treated with triphenylstannane in decalin at 25 °C the yields of hydrocarbons



were poor and erratic, and the values of k_f calculated in the usual way [12] from the product ratios (using Ingold's estimate [4] of k_H 5 × 10^6 l mol^{-1} s^{-1}) varied over the range 4 × 10^7 to 8 × 10^7 s^{-1}. Similar experiments with 1-methylcyclopropylmethyl chloride and 2,2-dimethylcyclopropylmethyl chloride gave even less satisfactory results. The cause of these difficulties was revealed by control experiments in which 2-chlorobutane was reduced with triphenylstannane in the presence of either 2-methylbut-1-ene or hex-1-ene. Under the usual analytical conditions the recovery of olefin was poor, although it improved dramatically when the gas chromatograph was run at high temperatures. We conclude that triphenylstannane adds to terminal olefins by a homolytic mechanism [13] to give alkyltriphenylstannanes which may undergo thermal decomposition to regenerate alkenes.



It appears therefor ...enylstannane, because of its propensity to ...minal olefins, is an unsuitable reagent fo... ...ve determination of the rates of ring op... ... primary cycloalkylmethyl radicals. ... rate constant (k_f *ca.* 6 × 10^7 s^{-1} at 2 ...ement of the cyclopropylmethyl r... ...ugh in satisfactory agreement with some of the earlier data, must therefore be regarded as a lower limit.

The reduction of the secondary chloride (11b) with triphenylstannane proceeded much more satisfactorily (see Table 1). Yields of products were uniformly high and the data obtained at different stannane concentrations give consistent values of k_t/k_H. Unfortunately, the value of k_H at 0 °C is not known. However, on the basis of the reasonable assumption [14] that log A for the hydrogen-atom transfer step is *ca.* 8.5, k_H is estimated to be 3.5 × 10^6 l mol^{-1} s^{-1} at 0 °C. It follows that at 0 °C the radical (12b) has k_f *ca.* 7 × 10^6 s^{-1}, a value considerably lower than that for the parent radical (12a) which probably lies in the upper part of the range 2.5—5.0 × 10^7 s^{-1} at this temperature. Possibly the difference between the rates of β-fission of the secondary (12b) and primary (12a) radicals reflects the greater thermodynamic stability of the former, but conformational effects may also be important.

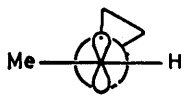
TABLE 1

Reduction of (1-chloroethyl)cyclopropane (11b) with Ph_3SnH in decalin at 0 °C

$[Ph_3SnH]_0$[a]/ mol l^{-1}	Relative yield (%) (13b)	*trans*-(15b)	*cis*-(15b)	*trans* : *cis*	Total yield (%)	$k_t k_H^{-1}$/ mol l^{-1}
1.49	43.4	46.3	10.3	4.5	83	1.96
1.16	37.7	51.7	10.7	4.8	81	1.90
0.30	13.4	69.7	16.9	4.1	82	1.94
0.14[b]	0.5	68.7	30.8	2.2	44	

[a] Initial concentration; Ph_3SnH present in large excess. [b] Initial concentration of Bu_3SnH.

Another indication of the role of conformational factors is given by the fact that *trans*-pent-2-ene is formed in greater yield than its *cis*-isomer. Experiments involving triphenylstannane gave a *trans* : *cis* ratio of *ca.* 4.5 but a separate experiment showed that each of the pure olefins undergoes isomerisation under the normal conditions to give an equilibrium mixture with *trans* : *cis* 4.8. Reactions conducted with tributylstannane at low concentration and an excess of halide do not suffer from this defect; consequently the value of the *trans* : *cis* ratio (2.2) obtained under these conditions correctly represents the relative proportions of isomers arising directly from the β-fission process. Undoubtedly, the predominance of the *trans*-product reflects the greater stability of the transition state derived from the *transoid*-conformation (16) as compared with that derived from the *cisoid*-conformation (17) in which non-bonded interactions are more severe.



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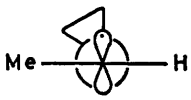


(17)

Control experiments, similar to those described above, showed that the vinylcyclohexane derivatives (22a), (22b), and (24b), formed by β-fission of the bicyclic radicals

(19a and b), could be recovered quantitatively from reactions involving triphenylstannane. It appeared, therefore, that a study of these and related radicals might afford useful information concerning substituent effects on the rates of cyclopropylcarbinyl rearrangements. However, as the data in Tables 2 and 3 indicate, these

TABLE 2

Reduction of *exo*-7-chloromethylbicyclo[4.1.0]heptane (18a) with Ph_3SnH at 25 °C [a]

$[Ph_3SnH]_o$[b]/ mol l^{-1}	Relative yield (%) (20a)	(22a)	Total yield (%)	$k_t k_H^{-1}$/ mol l^{-1}
1.71 [c]	1.55	98.45	100	54 ± 2
2.11	3.8	96.2	36	53 ± 6
3.10	4.9	95.1	40	60 ± 6
3.28	4.8	95.2	39	64 ± 3

[a] Reactions conducted in pentane unless otherwise specified. [b] Initial concentration; Ph_3SnH present in large excess. [c] Reaction conducted in decalin; chloro-compound in 10% excess.

systems also proved to be unsatisfactory for quantitative work. The relative yields of products containing an intact cyclopropane ring were so small, even at high triphenylstannane concentration, as to make *accurate* determination of the values of k_t/k_H impossible. Nevertheless, the results obtained reveal some interesting features. For example, the value of k_t/k_H (*ca.* 60 mol l^{-1} at 25 °C) for radical (19a) corresponds to a rate constant k_f of *ca.* 3×10^8 s^{-1}. The fact that this is larger than that for the cyclopropylmethyl radical (12a) at the same temperature probably reflects the greater strain energy of the bicyclic system.

The value of the rate constant for β-fission of the bicyclic radical (19a) at 0 °C can be estimated on the assumption that the activation energy is the same as that (5.9 kcal mol^{-1}) [2] for rearrangement of the cyclopropylmethyl radical. This gives a reasonable value of log *A* (12.8), and k_f *ca.* 1.2×10^8 s^{-1} at 0 °C. Comparison can now be made with the data for the radical (19b) after an appropriate statistical correction is made to the data for radical (19a) because of its symmetry. The rate constant

TABLE 3

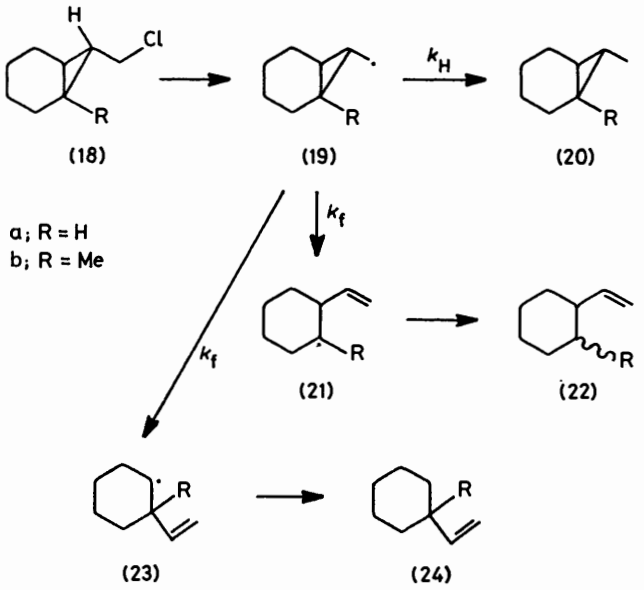
Reduction of *exo*-7-chloromethyl-1-methylbicyclo[4.1.0]-heptane (18b) with Ph_3SnH at 0 °C in pentane

$[Ph_3SnH]_o$[a]/ mol l^{-1}	Relative yield (%) (20b)	(24b)	*cis*-(22b)	*trans*-(22b)	*trans* : *cis*	Total yield (%)	$k_t k_H^{-1}$/ mol l^{-1}
0.66	1	24	27	48	1.8	34	*ca.* 65
1.06	2	23	26	50	1.9	28	*ca.* 52
ca. 1.2	2	24	25	50	2.0	32	*ca.* 59

[a] Initial concentration; Ph_3SnH present in large excess.

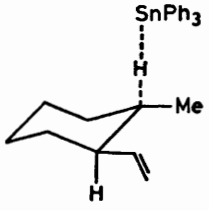
for fission of the less substituted βγ-bond in (19b) to give the radical (23b) has a value (*ca.* 5×10^7 s^{-1}) within experimental error of that (*ca.* 6.0×10^7 s^{-1}) for the fission of each bond in the unsubstituted radical (19a). However, the value of the rate constant for fission of the more substituted bond in (19b) has a value (*ca.* 1.5×10^8 s^{-1}) which is considerably larger. Thus the radical (19b) behaves as expected on thermochemical grounds [14] and affords the tertiary radical (21b) much more rapidly than the secondary (23b).

Within experimental error the ratio of *trans*-2-methylvinylcyclohexane *trans*-(22b) to *cis*-2-methylvinylcyclohexane *cis*-(22b) formed from the radical (21b) is independent of stannane concentration and has a value (1.9) similar to that for the reaction of 1,2-dimethylcyclohexyl radical with tributylstannane.[15] The preferred formation of the *trans*-compound *trans*-(22b) suggests



that the transition state is product-like (25), involving considerable deviation from planarity at the radical centre, and that the dominant factor controlling the outcome of the reaction is the tendency of the methyl substituent to occupy the less hindered pseudo-equatorial position.

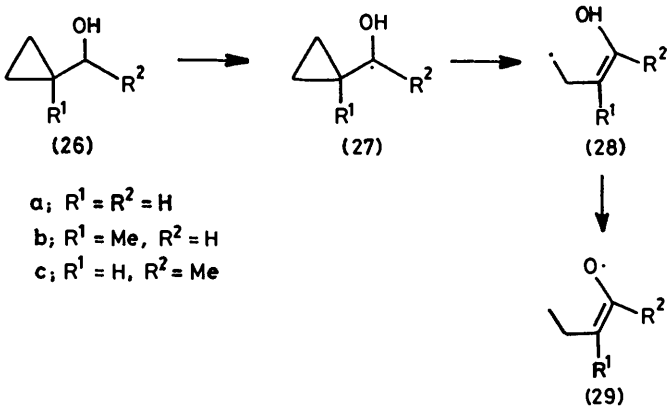
E.s.r. Studies of the Cyclopropylmethyl–Allylmethyl Radical Rearrangement.—Exploratory experiments were conducted with the aim of ascertaining whether e.s.r. measurements utilizing the flow system [16] could be helpful in studying cyclopropylmethyl radical rearrangements. When cyclopropanemethanol (26a) was mixed in the usual way [17] with titanous chloride and hydrogen peroxide in water two radicals were detected: that in higher concentration was 4-hydroxybut-3-enyl radical



(25)

(28a) formed by β-fission of the cyclopropylmethyl radical (27a) whilst that formed in much less amount was the enoxyl radical (29a) arising by 1,5-hydrogen atom transfer in the former.[11,18] A similar result was obtained when the radical (27a) was generated by reduction of cyclopropanecarbaldehyde with carbon dioxide radical anion.[19] It is noteworthy that only the enoxyl radical

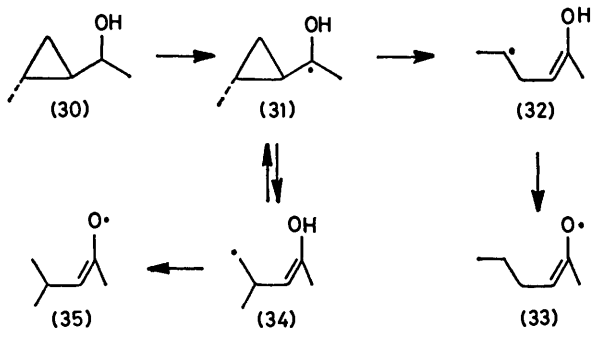
(29a) is observed when the radical (27a) is generated in cyclopropane solvent at temperatures approaching those employed here.[11,18] The most likely explanation for the difference in behaviour between the aqueous system and that using cyclopropane solvent is that the radical (28a)



a; $R^1 = R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = H$, $R^2 = Me$

is stabilised in water by hydrogen bonding of the hydroxy-group and undergoes hydrogen-atom transfer more slowly than it does in hydrocarbon solvents. It is pertinent that hydroxylic solvents accelerate the formation of hydroxy-substituted biradicals from photochemically excited ketones in a hydrogen-atom transfer reaction which is formally the reverse of that recorded here.[20]

1-Methylcyclopropanemethanol (26b) and α-methylcyclopropanemethanol (26c) behaved similarly when treated with titanous chloride and hydrogen peroxide in water. In each case the spectrum consisted of a strong signal for the initial rearrangement product (28b or c), and a much weaker one for the appropriate enoxyl radical (29b or c). Similar treatment of the *trans*-2-methyl compound (30) generated a very complex spectrum indicating the presence of at least four different radicals. The strongest signal was attributed to the secondary radical (32). The signal of the primary



radical (34) was very much weaker as were those attributed to the appropriate enoxyl radicals (33) and (35).

The results obtained from treatment of the alcohol (30) with hydroxyl radicals in water differ from those reported [11] for the radical (31) when generated in cyclopropane solvent. In the latter case only the primary radical (34) is detected at low temperature whilst the corresponding enoxyl radical (35) is formed at higher temperatures. One possible explanation is that in cyclopropane solvent the radical (34) which is the kinetically favoured β-fragmentation product, undergoes 1,5-hydrogen-atom transfer more rapidly than equilibration. However, in water 1,5-hydrogen-atom transfer is a relatively slow process, and competes inefficiently with formation of the thermodynamically favoured radical (32) *via* the sequence (34) ⟶ (31) ⟶ (32).

These experiments indicate that e.s.r. studies utilising the flow system are unlikely to be applicable to rigorous scrutiny of the rearrangement of cyclopropylmethyl radicals because of the tendency of the initial rearrangement products to undergo equilibration and other further reactions.

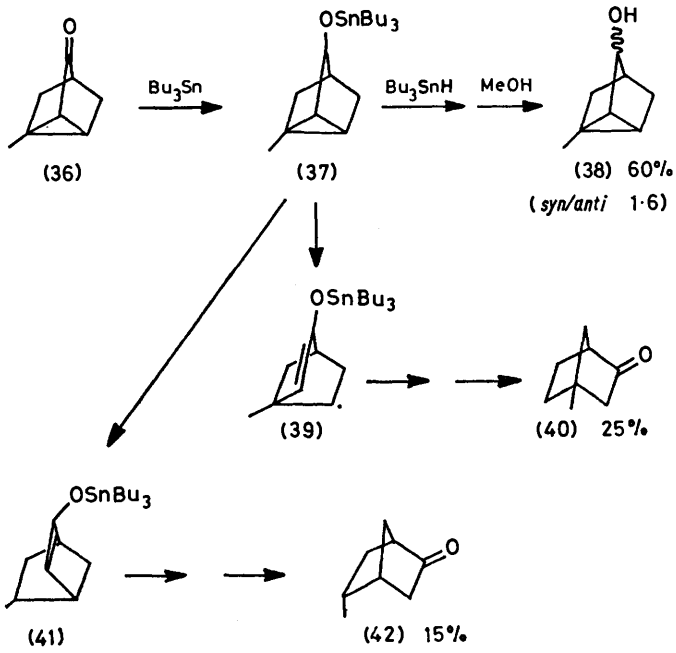
Radical Rearrangements in the Nortricyclene System.— We referred above to suggestions [10,11] that the unexpected preference shown by cyclopropylmethyl radicals containing a *trans*-methyl substituent [*e.g.* (5) or (6)] to undergo rearrangement by fission of the less substituted βγ-bond may reflect polar or conformation effects. In an attempt to distinguish between these possibilities we have examined the behaviour of radicals in which the rigid framework of the system maintains the semi-occupied orbital in the same relative disposition with respect to each of the two cyclopropane bonds potentially capable of undergoing fission.

Treatment of the ketone (36) with tributylstannane followed by methanolysis of the initial products afforded the compounds (38), (40), and (42) in yields given in the Scheme, which also shows the mechanism.[21] The fact that the major rearrangement product is the ketone (40) demonstrates that the radical (37) preferentially undergoes ring-opening by fission of the less substituted βγ-bond to afford the less stable possible product radical (39). Similarly, the radical (43), generated by treatment of the alcohol (38) with di-t-butyl peroxide afforded the ketone (36) and the two rearrangement products (40) and (42). In this case the preference for formation of the product (40) arising *via* the less exothermic pathway was small, possibly because the relatively high reaction temperature facilitates equilibration of the ring-opened radicals. An attempt to generate the radical (43) by photolysis of the ketone (36) in propan-2-ol gave a complex reaction mixture which could not be satisfactorily resolved.

Finally, we attempted to ascertain the direction of kinetically controlled fission of the unsubstituted radical (44). However, treatment of either *syn*- or *anti*-3-chloro-1-methylnortricyclene afforded a mixture of three hydrocarbons (46), (47), and (49) of which that derived from the more stable tertiary radical (45) was the major component. The product distribution was found to be independent of stannane concentration indicating that the equilibrium (45) ⇌ (44) ⇌ (48) is attained under these conditions (Table 4). An attempt to establish kinetic control by conducting the reaction with a high

concentration of triphenylstannane failed because of the reactivity of the products towards further attack by stannane.

In general our results accord best with the hypothesis [10,11] that polar effects are important in the β-fission of cyclopropylmethyl radicals. In particular, when there is an oxygen substituent at the radical centre the transition state should have dipolar character (50) and the fission of the less substituted βγ-bond should be facilitated. If, as has been suggested,[8] the rearrangement of cyclopropylmethyl radicals involves initially an interaction between the semi-occupied orbital and the vacant σ* orbital of the bond undergoing cleavage then a fractional positive charge will be generated at the radical centre, and the transition state will have dipolar character even in the absence of polar substituents. The development of such polarity could account for the abnormal mode of fission of *trans*-2-methylcyclopropylmethyl radical. However, the testing of this hypothesis awaits the development of convenient methods for the accurate determination of the rates of rearrangement of substituted cyclopropylmethyl radicals.



SCHEME

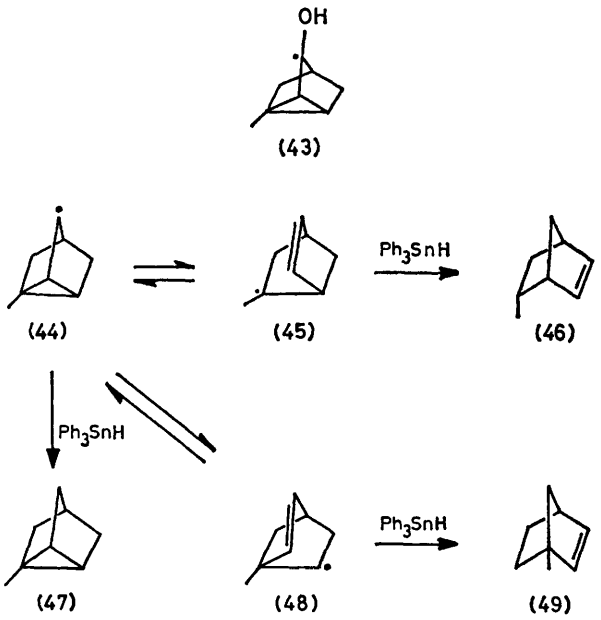
TABLE 4

Reduction of 3-chloro-1-methylnortricyclene with Bu_3SnH in hexane

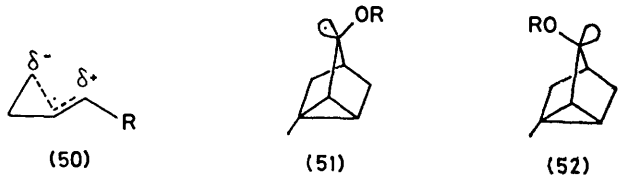
T/°C	Isomer	$[Bu_3SnH]_0$/ mol l^{-1}	Relative yield (%) (47)	(49)	(46) [a]	Total yield (%)
60	*syn*	0.10	14.8	9.0	76.1	78.6
60	*syn*	0.05	14.5	9.1	76.4	85.6
60	*anti*	0.01	14.6	9.0	76.4	86.7
80	*syn*	0.01	16.8	9.9	73.3	68.3
100	*syn*	0.01	17.9	10.7	71.4	86.5

[a] The *exo*-isomer was formed in <3% yield.

There remains the question of the validity of our assumption that the semi-occupied orbital in the radicals (37) and (43) is symmetrically disposed with respect to the cyclopropane ring. In the light of previous work with structurally related bicyclic radicals,[22] and radicals bearing an α-oxygen substituent [23] it appears possible that such radicals may exist in two rapidly interconverting conformers (51) and (52), of which the former will be favoured on steric grounds. Application of orbital overlap criteria [8] suggests that ring-opening of the more stable conformer (51) should occur by fission of the less substituted βγ-bond. Nevertheless, it seems unlikely that the barrier to interconversion of the conformers (51) and (52) would be sufficiently large to account for the observed preference for formation of radicals such as (39).

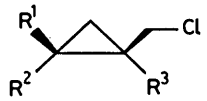


Synthetic Methods.—Most compounds required as radical precursors or for comparison with products were prepared by established methods. However, the facility with which some cyclopropylmethyl chlorides undergo rearrangement prompted us to develop mild procedures for the preparation of such compounds from the related alcohols. The method which gave least rearrangement (<3%) involved treatment of the alcohol with thionyl chloride in butane at −78 °C. It was used for the preparation of the chlorides (53)—(57). The secondary chloride (11b) was readily prepared by treatment of the appropriate alcohol with phosphorus pentachloride in pentane at −20 °C but this method, like all others

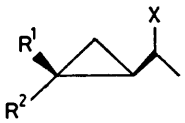


attempted, was unsuccessful when applied to the preparation of the secondary chloride (58).

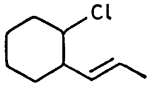
All procedures employed for the preparation of the bicyclic chloride (18a) from the appropriate alcohol afforded also considerable quantities (8—25%) of the unsaturated isomer (59), presumably *via* a carbonium ion mechanism. The required chloride (18a) was too unstable to withstand purification by preparative g.l.c. or distillation through a spinning-band column. Eventually it was isolated by ozonolysis of the mixture which destroyed the olefinic component (59) and allowed the chloride (18a) to be readily separated by distillation.



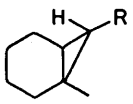
(53) $R^1 = R^2 = Me$; $R^3 = H$
(54) $R^1 = R^2 = H$; $R^3 = Me$
(55) $R^1 = Me$, $R^2 = R^3 = H$
(56) $R^1 = R^3 = H$, $R^2 = Me$



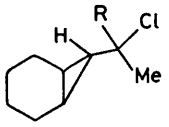
(57) $R^1 = H$, $R^2 = Me$
(58) $R^1 = R^2 = Me$



(59)



(60) R = CH_2OH
(61) R = CO_2Me



(62) R = H
(63) R = Me

The bicyclic chloride (18b) was similarly obtained from the *exo*-alcohol (60). The configuration of the alcohol (60) and the ester (61) was assigned on the basis of the similarity of their n.m.r. spectra to those of related compounds of known stereochemistry. Because of their lability neither of the chlorides (62) and (63) could be obtained in purity adequate for kinetic work.

EXPERIMENTAL

General experimental details have been given previously.[24] The following columns were used for g.l.c.: (*a*) 3 m × 7 mm 14% Carbowax 20M-TPA on Chromasorb A glass column, (*b*) 6.3 m × 3.2 mm 0.75% FFAP on Varaport 30 metal column, (*c*) 6 m × 8 mm 30% QF1-NPGS (2 : 1) on Chromasorb A glass column, (*d*) 4.6 m × 2.1 mm 5% Apiezon M on Varaport 30 glass column, (*e*) 2 m × 7 mm 20% QF1 on Varaport 30 glass column, (*f*) 70 m × 0.5 mm Carbowax 20M surface coated open tubular glass column, (*g*) 1.4 m × 7 mm 17% FFAP on Varaport 30 glass column, (*h*) 3 m × 3.2 mm 20% dimethylsulpholan on Chromasorb W glass column, (*i*) 70 m × 0.5 mm squalane surface coated open tubular glass column, (*j*) 6 m × 3.2 mm 20% propylene carbonate on Varaport 30 glass column, (*k*) 2 m × 3.2 mm 40% $AgNO_3$–benzyl cyanide on Chromasorb W metal column.

Chloromethylcyclopropane.—Treatment of cyclopropanemethanol with thionyl chloride in ether [25] afforded the chloride, b.p. 84—85 °C. The sample used for kinetic work was further purified by preparative g.l.c. [column (*a*) 90 °C].

2-*Chloromethyl*-1,1-*dimethylcyclopropane* (53).—2,2-Dimethylcyclopropanemethanol [26] (2.0 g), prepared by reduction of 2,2-dimethylcyclopropanecarboxylic acid [27] with lithium aluminium hydride, was stirred in butane (20 ml) at −78 °C while thionyl chloride (2.3 g) was added in one portion. After being stirred for 5 min at −78 °C the mixture was concentrated *in vacuo* at 0 °C and the residual oil was distilled to afford the required chloride (1.9 g, 82%), b.p. 55—60 °C at 100 mmHg, δ 0.6—1.8 (3 H, complex, ring H), 1.08 (3 H, s, CH_3), 1.12 (3 H, s, CH_3), and 4.05 (2 H, m, CH_2Cl). Analytical g.l.c. and the n.m.r. spectrum revealed the presence of 3% of an unsaturated chloride tentatively identified as 4-chloro-2-methylpent-1-ene, which could not be removed by preparative g.l.c. because of the lability of the required compound.

1-*Chloromethyl*-1-*methylcyclopropane* (54).—Application of the foregoing procedure to 1-methylcyclopropanemethanol [28] afforded the required chloride (1.5 g, 82%), b.p. 32—35 °C at 30 mmHg, n_D^{20} 1.433 5 (lit.,[29] n_D^{20} 1.432 9).

cis- *and* trans-1-*Chloromethyl*-2-*methylcyclopropane* (55) *and* (56).—Crotyl alcohol (10.2 g; *cis* : *trans* 2 : 1) was added to a stirred suspension of zinc–copper couple (prepared from 27.5 g of zinc powder [30]) in ether (150 ml) and di-iodomethane (70 g) and the mixture was heated under reflux for 2 h. Extraction of the crude product with ether and distillation afforded a mixture of *cis*- and *trans*-2-methylcyclopropanemethanol (10.0 g, 82%), b.p. 95—100 °C at 15 mmHg. Preparative g.l.c. [column (*a*); 130 °C] afforded pure samples of each isomer which had n.m.r. spectra identical to those previously reported.[31]

Treatment of a sample (2.0 g) of the mixture of alcohols with thionyl chloride as described above, gave a mixture of *cis*- and *trans*-1-chloromethyl-2-methylcyclopropane (1.7 g, 72%), pure samples of which, with properties identical to those previously reported,[28] were isolated by preparative g.l.c. [column (*a*), 80 °C].

trans-1-*Chloro*-1-(2-*methylcyclopropyl*)*ethane* (57).—Cyclopropanation of *trans*-pent-2-en-3-ol (12 g) as in the foregoing experiment afforded *trans*-α,2-dimethylcyclopropanemethanol [32] (10.0 g, 79%), b.p. 87—89 °C at 100 mmHg, as a 1 : 1 mixture of the two possible diastereoisomers. A sample (1.6 g) of the alcohol, when treated with thionyl chloride in butane in the usual way, gave a mixture of the two diastereoisomers of trans-1-*chloro*-1-(2-*methylcyclopropyl*)*ethane* (0.8 g, 44%), preparative g.l.c. [column (*a*) 120 °C] of which gave one pure diastereoisomer (Found: C, 61.3; H, 9.6. $C_6H_{11}Cl$ requires C, 60.8; H, 9.4%), δ 0.3—1.2 (3 H, complex, ring H), 1.1 (3 H, d, *J* 5 Hz, CH_3), 1.6 (3 H, d, *J* 6 Hz, CH_3), and 3.4 (1 H, m, CHCl). The second diastereoisomer had an identical n.m.r. spectrum apart from a small variation in the pattern in the region δ 0.3—1.2.

α,2,2-*Trimethylcyclopropylmethanol*.—Reduction of 1-acetyl-2,2-dimethylcyclopropane [33] with lithium aluminium hydride afforded the required alcohol as a mixture (10 : 1) of two diastereoisomers [34] (2.7 g, 95%), b.p. 61—62 °C at 20 mmHg (Found: C, 73.8; H, 12.3. $C_7H_{14}O$ requires C, 73.6; H, 12.4%).

Treatment of the alcohol with either phosphorus pentachloride in pentane at −20 °C or with thionyl chloride in butane at −78 °C gave a mixture of unsaturated chlorides, the major component of which has been tentatively identified as 5-chloro-5,5-dimethylhex-2-ene, δ 1.5 (6 H, s, 2 × CH_3), 1.7 (3 H, m, CH_3), 2.4 (2 H, m, CH_2), and 5.6 (2 H, m, CH=CH).

1-*Chloro*-1-*cyclopropylethane* (11b).—1-Cyclopropyleth-

anol (6.2 g) was treated in the usual way [35] with phosphorus pentachloride in pentane to afford a mixture of (5.6 g, 74%) of the required chloride (95%) and 5-chloropent-2-ene (5%) from which a pure sample of the former was isolated by preparative g.l.c. [column (*a*), 50 °C].

exo-*Bicyclo*[4.1.0]*heptan*-7-*ylmethanol*.—A solution of (trimethyl phosphite)copper(I) iodide [36] (650 mg) and benzoyl peroxide (260 mg) in cyclohexene (250 ml) was boiled under reflux whilst ethyl diazoacetate (35 g) in cyclohexene (250 ml) was slowly added. After being heated for 18 h the mixture was cooled, filtered, and distilled to afford a mixture of the *exo*- and *endo*-isomers (10 : 1) of ethyl bicyclo[4.1.0]-heptane-7-carboxylate (41 g, 69%), b.p. 86—88 °C, which was saponified with aqueous sodium hydroxide. Two recrystallizations of the product from hexane gave pure (> 99.5%) *exo*-bicyclo[4.1.0]heptane-7-carboxylic acid [37] (23 g, 75%), m.p. 97—99 °C. Reduction of a sample (10 g) of this acid with lithium aluminium hydride in ether gave the required alcohol [38] (7.7 g, 85%), b.p. 92—93 °C at 8.5 mmHg, the purity of which was established by g.l.c. [column (*b*), 150 °C].

exo-7-*Chloromethylbicyclo*[4.1.0]*heptane* (18a).—Thionyl chloride (5.0 g) was added to a solution of the foregoing alcohol (5.2 g) in ether (20 ml) at −78 °C. After 10 min the solvent was removed by evaporation *in vacuo* at 0 °C and the residue, dissolved in pentane, was passed through a short column of calcium carbonate. Distillation of the eluate afforded a mixture (5.2 g, 89%), b.p. 39—41 °C at 1.2 mmHg which was shown by g.l.c. [column (*b*), 110 °C] to contain *ca.* 75% of the required chloride and 25% of 1-chloro-2-vinylcyclohexane.

A sample (2.7 g) of the chloride mixture in dichloromethane (50 ml) was treated at −78 °C with ozone in oxygen until the solution developed a permanent blue colour. Hexamethylphosphoric triamide (2 g) was then added, and the solvent was removed by evaporation *in vacuo* at 0 °C. The residual oil was dissolved in pentane, washed repeatedly with iced water, and distilled to afford pure [g.l.c. column (*b*), 110 °C] exo-7-*chloromethylbicyclo*[4.1.0]*heptane*, b.p. 40 °C at 1.0 mmHg, n_D^{22} 1.4482 (Found: C, 66.7; H, 9.0. $C_8H_{13}Cl$ requires C, 66.4; H, 9.1%), δ 0.7—2.5 (11 H, complex, ring H) and 3.5 (2 H, d, *J* 7 Hz, CH_2Cl).

Treatment of the *exo*-alcohol with triphenylphosphine and *N*-chlorosuccinimide or of its toluene-*p*-sulphonate with pyridinium chloride in dimethylformamide gave similar mixtures from which the required chloride could be isolated after ozonation.

exo-1-*Methylbicyclo*[4.1.0]*heptan*-7-*ylmethanol*.—When 1-methylcyclohexene (31 g) in methylcyclohexane (400 ml) was treated with ethyl diazoactate as described above the product comprised a mixture (38 g, 65%) of *exo*- and *endo*-isomers (77 : 22), preparative g.l.c. [column (*c*), 180 °C] of which afforded a sample of pure ethyl *exo*-1-methylbicyclo-[4.1.0]heptane-7-carboxylate, b.p. 85 °C at 2.5 mmHg (Found: C, 72.2; H, 10.2. $C_{11}H_{18}O_2$ requires C, 72.5; H, 10.0%), $\lambda_{max.}$ 1 720 cm^{-1}, δ 1.1—2.2 (16 H, complex) and 4.2 (2 H, q, CH_2O).

The ester mixture was saponified with aqueous sodium hydroxide and the product was cyrstallised three times from hexane to afford pure (> 99%) *exo*-1-methylbicyclo[4.1.0]-heptane-7-carboxylic acid,[39] m.p. 121—124 °C, a sample (8 g) of which was reduced with lithium aluminium hydride in ether. The usual work-up gave the required exo-*alcohol* (6.8 g, 93%), b.p. 82—85 °C at 3.5 mmHg (Found: C, 76.8; H, 11.6. $C_9H_{16}O$ requires C, 77.0; H, 11.5%), $\lambda_{max.}$ 3 370 cm^{-1}, δ 0.3—2.1 (11 H, complex), 1.1 (3 H, s, CH_3), and 3.6 (2 H, m, appears as the AB portion of an ABX system with J_{AB} 10 Hz, CH_2OH). The compound was shown to be homogeneous by g.l.c. [column (*b*), 160 °C]. The assignment of configuration rests on the similarity of the n.m.r. pattern for the CH_2OH protons to that for similar compounds.[40]

exo-7-*Chloromethyl*-1-*methylbicyclo*[4.1.0]*heptane* (18b).—The foregoing alcohol (1.3 g) in tetrahydrofuran was added to the reagent formed from triphenylphosphine (2.1 g) and *N*-chlorosuccinimide (1.3 g) in tetrahydrofuran (45 ml) and the mixture was stirred at ambient temperature until most of the solid has dissolved (*ca.* 2 h). The mixture was then concentrated *in vacuo*, taken up in ether, washed with water, dried, and chromatographed on Florisil to afford a mixture (0.8 g, 55%) of approximately equal parts of the required chloride and 1-chloro-1-methyl-2-vinylcyclohexane. Ozonation of a sample (0.7 g) of the mixture as described above gave pure [g.l.c. column (*d*), 120 °C] exo-7-*chloromethyl*-1-*methylbicyclo*[4.1.0]*heptane* (0.3 g), b.p. 80—81 °C at 4 mmHg, δ 0.4—2.2 (10 H, complex, ring H), 1.2 (3 H, s, CH_3), and 3.6 (2 H, m, J_{AB} 10 Hz, CH_2Cl). The assignment of configuration rests on the fact that the CH_2Cl protons like those of related exo-*compounds*,[40] appear as the AB portion of an ABX system.

exo- *and* endo-*Methyl* 1-*Methylbicyclo*[4.1.0]*heptane*-7-*carboxylate*.—The mother-liquors remaining after crystallisation of *exo*-1-methylbicyclo[4.1.0]heptane-7-carboxylic acid were evaporated and the residue was treated with ethereal diazomethane. Preparative g.l.c. [column (*e*), 140 °C] of the resultant crude ester gave (a) *methyl* exo-1-*methylbicyclo*[4.1.0]*heptane*-7-*carboxylate*, b.p. 70 °C (block) at 2 mmHg (Found: C, 71.8; H, 9.7. $C_{10}H_{16}O_2$ requires C, 71.4; H, 9.6%), δ 1.0—2.2 (10 H, complex ring H), 1.1 (3 H, s, CH_3), and 3.6 (3 H, s, CH_3); (b) *methyl* endo-1-*methylbicyclo*[4.1.0]*heptane*-7-*carboxylate*, b.p. 70° (block) at 2 mmHg (Found: C, 71.6; H, 9.9%), δ 0.9—2.2 (10 H, complex ring H), 1.06 (3 H, s, CH_3), and 3.6 (3 H, s, CH_3). In benzene the 1-methyl singlet of the *exo*-isomer resonates at δ 1.4 whilst that of the *endo*-isomer resonates at δ 1.06. The greater degree of deshielding for the methyl *cis* to a methoxycarbonyl group has adequate precedent.[40]

1-(exo-*Bicyclo*[4.1.0]*heptan*-7-*yl*)*ethanol*.— exo-7-Acetylbicyclo[4.1.0]heptane [41] (3.0 g), prepared by reaction of *exo*-bicyclo[4.1.0]heptane-7-carboxylic acid with methyllithium, was reduced with lithium aluminium hydride (1.3 g) in ether (20 ml) at ambient temperature for 16 h. The usual work-up afforded the required *alcohol* (3.0 g, 98%), b.p. 81—83 °C at 5 mmHg (Found: C, 77.2; H, 11.6. $C_9H_{16}O$ requires C, 77.2; H, 11.5%), $\lambda_{max.}$ 3 350 cm^{-1}, δ 0.3—2.1 (11 H, complex), 1.2 (3 H, d, *J* 7 Hz, CH_3), and 3.1 (1 H, m, CHO). The purity (>99%) of the compound was established by g.l.c. [column (*b*), 150 °C].

An attempt to convert the alcohol into its chloride by treatment with phosphorus pentachloride in pentane at −20 °C or with thionyl chloride in pentane at −78 °C gave only a mixture of the stereoisomers of 1-(2-chlorocyclohexyl)propene, b.p. 40 °C (block) at 1 mmHg (Found: C, 68.6; H, 9.6. $C_9H_{15}Cl$ requires C, 68.2; H, 9.5%), δ 0.9—2.5 (12 H, complex), 3.6 (1 H, m, CHCl), and 5.5 (2 H, complex, CH=CH).

2-(exo-*Bicyclo*[4.1.0]*heptan*-7-*yl*)*propan*-2-*ol*.— Treatment of methyl *exo*-bicyclo[4.1.0]heptane-7-carboxylate (2.5 g) with methylmagnesium iodide afforded the required alcohol (1.95 g, 78%), b.p. 45—50 °C at 0.2 mmHg, $\lambda_{max.}$

3 350 cm^{-1}, δ 0.4—2.2 (12 H, complex) and 1.1 (6 H, s, 2 × CH_3).

When this alcohol was treated with thionyl chloride in ether, or with phosphorus pentachloride in dichloromethane it afforded only an unsaturated compound tentatively identified as 1-(2-chlorocyclohexyl)-2-methylpropene. Treatment of the toluene-*p*-sulphonate of the alcohol with lithium chloride in hexamethylphosphoric triamide gave the same result.

1-*Methylnortricyclen*-3-*ol* (38).—Norborn-5-en-2-one [42] was converted as previously described [43] into the required alcohol, b.p. 82—83 °C at 8 mmHg, which was shown by g.l.c. [column (*f*), 150 °C] to be a mixture of isomers (*anti* : *syn* 5 : 1).

1-*Methylnortricyclen*-3-*one* (36).—Oxidation of the foregoing alcohol (6.2 g) with chromic acid by Brown's method [44] gave the ketone,[43] b.p. 98—100 °C at 25 mmHg, the purity (>98%) of which was established by g.l.c.

3-*Chloro*-1-*methylnortricyclene*.— 1-Methylnortricyclen-3-ol (2.0 g) was added to a stirred suspension of phosphorus pentachloride (3.1 g) in pentane (17 ml) at −20 °C. After 1 h iced water was added, and the pentane layer was washed with aqueous sodium hydrogencarbonate and with water. Evaporation of the dried pentane solution *in vacuo* gave the required chloride (2.1 g, 91%) as a mixture of *syn*- and *anti*-isomers (2 : 1) which were separated by preparative g.l.c. [column (*a*) 150 °C]. syn-3-*Chloro*-1-*methylnortricyclene* had n_D^{26} 1.484 0 (Found: C, 67.2; H, 7.7; Cl, 24.8. $C_8H_{11}Cl$ requires C, 67.4; H, 7.8; Cl, 24.9%), δ 1.0—1.45 and 1.8—2.1 (7 H, complex, ring H), 1.3 (3 H, s, CH_3), and 3.85br (1 H, s, CHCl). The anti-*isomer* had n_D^{26} 1.482 8, δ 1.1—1.4 and 1.5—2.2 (7 H, complex ring H), 1.15 (3 H, s, CH_3), and 3.9br (1 H, s, CHCl).

Reference Compounds.—But-1-ene, pent-2-ene, hex-1-ene, *cis*- and *trans*-pent-2-ene, and methylcyclopropane were commercial samples. The following compounds had physical constants in agreement with those previously reported: *exo*-7-methylbicyclo[4.1.0]heptane (20a),[44] prepared by reduction of the chloro-compound (18a) with lithium aluminium hydride; vinylcyclohexane,[45] prepared by a Wittig reaction on cyclohexanecarbaldehyde; ethylcyclopropane, prepared by Wolff–Kishner reduction of acetylcyclopropane; 1-methylnortricyclene (47), 1-methylnorbornene (49), and 5-methylnorbornene (46), by Wolff–Kishner reduction of the appropriate ketones.

A mixture of the *endo*-and *exo*-isomers of 5-methylnorbornan-2-one (42) and of the 6-methyl compound was obtained by hydroboration–oxidation of 5-methylnorbornene,[46] whilst a mixture of the *exo*-isomers of 5-methyl- and 6-methyl-norbornan-2-one was available from hydrogenation of *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-6-one.[47] The identification of isomers could be made on the basis of available g.l.c. data.[46,47] 4-Methylnorbornan-2-one [48] (40), m.p. 110—111 °C (Found: C, 77.8; H, 10.1. $C_8H_{12}O$ requires C, 77.4; H, 9.7%), was obtained as a byproduct from the preparation of 1-methylnorborn-5-en-2-one.[49]

1,7-*Dimethylbicyclo*[4.1.0]*heptane*.—Oxidation of a mixture of the *exo*- and *endo*-isomers of 1-methylbicyclo[4.1.0]-heptan-7-ylmethanol (1.0 g) with chromium trioxide and pyridine in methylene chloride [50] afforded a mixture of *exo*- and *endo*-1-methylbicyclo[4.1.0]heptane-7-carbaldehyde (0.53 g, 54%), b.p. 70 °C (block) at 15 mmHg (Found, C, 78.2; H, 10.7. $C_9H_{14}O$ requires C, 78.2; H, 10.2%). Wolff–Kishner reduction of the aldehyde gave 1,7-dimethylbicyclo-[4.1.0]heptane, n_D^{20} 1.452 0 (Found: C, 87.4; H, 13.0. C_9H_{16} requires C, 87.0; H, 13.0%), as a mixture of isomers (*exo* : *endo* 4 : 1) which were isolated by preparative g.l.c. [column (*a*), 80 °C].

trans-1-*Methyl*-2-*vinylcyclohexane*.—A Wittig reaction of *trans*-2-methylcyclohexanecarbaldehyde [51] and methyltriphenylphosphorane gave the required olefin as a mixture of isomers (*trans* : *cis* 15 : 1), preparative g.l.c. [column (*g*), 80 °C] of which gave pure trans-1-*methyl*-2-*vinylcyclohexane*, n_D^{23} 1.443 8 (Found: C, 87.3; H, 12.9. C_9H_{16} requires C, 87.0; H, 13.0%), δ 0.8—2.0 (13 H, complex), 4.8—5.2 (2 H, m, $=CH_2$), and 5.3—6.0 (1 H, m, =CH).

cis-1-*Methyl*-2-*vinylcyclohexane*.—Oxidation of *cis*-2-methylcyclohexylmethanol [52] with chromium trioxide and pyridine in dichloromethane [50] gave a mixture of isomers (*cis* : *trans* 5 : 1) of 2-methylcyclohexanecarbaldehyde from which a mixture of isomers (*cis* : *trans* 20 : 1) of the required olefin was obtained by a Wittig reaction. Preparative g.l.c. [column (*g*), 80 °C] gave pure cis-1-*methyl*-2-*vinylcyclohexane*, n_D^{22} 1.451 9 (Found: C, 87.2; H, 12.7. C_9H_{16} requires C, 87.0; H, 13.0%), 1.85 (3 H, d, *J* 7 Hz, CH_3), 1.5br (10 H, s, ring H), 4.8—5.2 (2 H, m, $=CH_2$), and 5.6—6.3 (1 H, m, =CH).

1-*Methyl*-1-*vinylcyclohexane*.—1-Methylcyclohexanecarbaldehyde, prepared by oxidation of 1-methylcyclohexylmethanol,[53] was treated with methyltriphenylphosphorane in the usual way to give 1-methyl-1-vinylcyclohexane,[53] b.p. 136 °C. Preparative g.l.c. [column (*g*), 80 °C] gave a pure sample n_D^{20} 1.456 5, δ 0.95 (3 H, s, CH_3), 1.4br (10 H, s, ring H), 4.7—5.2 (2 H, m, $=CH_2$), and 5.7—6.0 (1 H, dd, *J* 17 and 9 Hz, =CH).

Reductions of Chloro-compounds with Triphenylstannane.—General details of the experimental method have been given previously.[54] The monocyclic chloro-compounds were isolated by preparative g.l.c. immediately before use to ensure their purity. Irradiation with a sun lamp of ampoules containing the reaction mixtures was employed to ensure efficient initiation of the free radical reactions. After 24 h the reactions were quenched and the products determined by quantitative g.l.c. Columns (*d*), (*h*), and (*i*) were used for the separation of vinylcyclohexanes, and columns (*j*) and (*k*) for acyclic olefins. The total yield of hydrocarbon products from reactions involving the bicyclic chloro-compounds (18a and b) which used triphenylstannane in large excess was low (30—40%). In these cases an amount of unchanged chloro-compound consistent with the observed yield could be detected by g.l.c.

Control Experiments.—2-Chlorobutane was reduced with triphenylstannane in the presence of samples of the following representative olefins: hex-1-ene, 2-methylbut-1-ene, pent-2-ene, vinylcyclohexane, and *trans*-1-methyl-2-vinylcyclohexane. The first two olefins were consumed whereas the others were recovered quantitatively. However, *cis*- and *trans*-pent-2-ene were each converted under these reaction conditions into the same equilibrium mixture of geometrical isomers.

Results.—The yields of but-1-ene and methylcyclopropane obtained when chloromethylcyclopropane was reduced at 25 °C in decalin were erratic. The following representative data for reactions involving a large excess of triphenylstannane are given in the order $[Ph_3SnH]_0$, relative yield of methyl cyclopropane, relative yield of but-1-ene, total yield (%), k_t/k_H: (*a*) 0.38M, 2.5%, 97.2%, 63%, 14.8 l mol^{-1}; (*b*) 0.76M, 5.8%, 94.2%, 71%, 12.3 l mol^{-1}; (*c*) 1.52M, 15.3%, 84.7%, 81%, 8.4 l mol^{-1}. The results of reactions with other substrates are given in Tables 1—4.

Reduction of 1-*Methylnortricyclen*-3-*one* (36) *with Tributylstannane*.—A mixture of the ketone (110 mg) and tributylstannane (520) at 25 °C was irradiated with a sunlamp for 24 h.[21] The mixture was then treated with methanol and the products (96%) determined by g.l.c. [column (*f*), 150 °C]. The results are given in the Scheme.

Reaction of 1-*Methylnortricyclen*-3-*ol* (38) *with Di-t-butyl Peroxide*.—A mixture of the alcohol (150 mg) and the peroxide (25 mg) was heated in a sealed tube at 140 °C for 24 h. The products (95%), determined by g.l.c. [column (*f*), 150 °C] were: 1-methylnortricyclen-3-one (67%), 4-methylnorbornan-2-one (17%), and 5-methylnorbornan-2-one (16%).

E.s.r. Spectroscopy.—An aqueous solution of the appropriate alcohol or ketone (4 ml l^{-1}) was mixed in the cavity with solutions of reagents for the generation of hydroxyl radicals or carbon dioxide radical anion as previously described.[17,19] Characteristics of the spectra recorded for the various substrates were as follows:

Cyclopropylmethanol.—The spectrum recorded when this alcohol reacted with hydroxyl radicals comprised a strong signal for the 4-hydroxybut-3-enyl radical (28a), $a(H_\alpha)$ 22.1, $a(H_\beta)$ 28.5 G, g 2.002 6, and a much weaker signal the characteristics of which could not be accurately determined but which corresponded approximately with those reported [11] for the enoxyl radical (29a). The same spectrum was recorded when carbon dioxide radical anion was generated in the presence of cyclopropanecarbaldehyde.

1-*Methylcyclopropylmethanol*.—The spectrum comprised overlapping signals for the 3-methyl-4-hydroxybut-3-enyl radical (28b), $a(H_\alpha)$ 22.1, $a(H_\beta)$ 27.1 G, g 2.002 6, and the corresponding enoxyl radical (29b), $a(CH_3)$ 21.2, $a(CH_2)$ 13.2, a(CHO) 2.9 G, g 2.004 4.

α-*Methylcyclopropylmethanol*.—This alcohol gave a strong signal for the radical (28c), $a(H_\alpha)$ 22.0, $a(H_\beta)$ 28.8 G, g 2.002 6, and a very weak signal with features similar to those [11] of the enoxyl radical (29c).

trans-α,2-*Dimethylcyclopropylmethanol*.—The spectrum comprised overlapping signals for four different radicals. The two stronger signals were identified as arising from the primary radical (34), $a(H_\alpha)$ 21.5, $a(H_\beta)$ 24.0, g 2.002 6, and the secondary radical (32), $a(H_\alpha)$ 21.2 G, $a(CH_2)$ 21.2, $a(CH_3)$ 25.2 G, g 2.002 6. The remaining signals which were very weak appeared to have characteristics similar to those reported for the two enoxyl radicals (33) and (35).

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