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THE CYCLOPROPYL RADICAL

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CONTENTS

INTRODUCTION

A useful model for the description of bonding in cyclopropane is that proposed by Coulson and Moffit.[1] In this model two pairs of hybridized orbitals are used, one pair for the *endo* bonds and the other pair for the *exo* bonds. The orbitals associated with the *endo* bonds were calculated to be $sp^{4.12}$ hybridized and those associated with the *exo* bond $sp^{2.28}$ hybridized. This hybridization corresponds to a bond angle of 104° for the *endo* orbitals and 116° for the *exo* orbitals. A refinement[2] of Coulson and Moffit's calculation suggest *endo* orbitals of sp^5 hybridization (angle 101°32′) and *exo* orbitals of $sp^{2.28}$ (angle 116°). The greater p-character of the *endo* bonds and the greater s-character associated with the *exo* bonds accounts for most of the physical and chemical properties associated with cyclopropane.[2] The molecule is highly strained with an estimated strain energy of 27.6 kcal/mole or 9.2 kcal/mole per CH_2 group. The strain is largely a result of bond angle distortion (Baeyer strain) and nonbonded repulsions (Pitzer strain).[3]

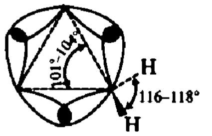
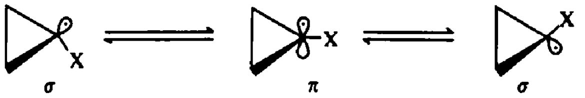


Fig. 1. *Exo* and *endo* bonds in cyclopropane

Going from cyclopropane to a planar cyclopropyl radical would relieve Pitzer strain (four H–H interactions), but it would also increase bond angle distortion thus resulting in greater internal strain (I-strain).[4] This latter effect may be one of the reasons for the observation that the cyclopropyl radical, in contrast to other cyclic or acyclic radicals, exists as a bent σ radical.[5,6] Delocalizing substituents ($x = \pi$ systems) attached to the radical site could convert the cyclopropyl σ radical to a π-radical. On the other hand, electronegative substituents (O, F) attached to a radical site have a tendency to convert what would ordinarily be a π radical to a σ radical.[6] Such substituents attached to the cyclopropyl radical site could reinforce the σ character of the radical and therefore possibly decrease the rate of inversion. Unless constrained, for example at a bridgehead, a σ radical such as cyclopropyl will invert configuration rapidly ($\sim 10^8 \, s^{-1}$), with inversion proceeding through a π radical transition state.

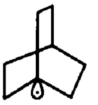
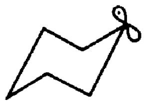
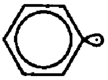
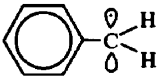


In general σ radicals, like cyclopropyl, are more electrophilic than π radicals.[7] The larger the s-character of an orbital, the greater the electronegativity of that orbital and the greater the electrophilic character.

REACTIVITY

Consistent with the σ nature of the cyclopropyl radical is its reactivity. In general, σ radicals are more reactive and less selective than π radicals. The 1-bicyclo[2.2.2]octyl radical, which should be a standard for σ radicals since it cannot invert its configuration, is the least selective. The benzyl radical, a delocalized π radical, is the most selective. The cyclohexyl radical, a non-delocalized π radical is intermediate in selectivity. The phenyl radical, a non-inverting σ radical in an sp^2 hybridized orbital shows greater selectivity than a non-inverting σ radical in sp^3 hybridized orbital. The cyclopropyl radical, an inverting σ radical in an $sp^{2.28}$ hybridized orbital, most nearly resembles the non-inverting phenyl σ radical but is more selective (less reactive). The reactivity data in Table 1 are those of Rüchhardt.[8] The significance of these experiments is that they minimize polar effects in the reaction of the radicals since the same leaving group, the CCl_3 radical, is involved in both radical abstraction reactions.

Table 1. Competition constant r for the reaction of R with $BrCCl_3$ and CCl_4[8]

R.	Type	T(°C)	r[a]
	σ	80	59
	π	11	566
	σ	110	278
	σ	104	184
	π	80	1700

[a] r = RBr/RCl

$$\cdot CCl_3 + RBr \xleftarrow{BrCCl_3} R\cdot \xrightarrow{CCl_4} R\text{-}Cl + \cdot CCl_3$$

From the relative reactivity data, shown in Table 2, which describes the thermal decomposition of biscyclopropanoyl peroxide is a series of substituted benzenes, Shono[9] has concluded that the cyclopropyl radical more closely resembles the phenyl[10] σ radical in its reactivity than it does the cyclohexyl[11] π radical. The 2-phenylcyclopropyl radical behaves similarly to the cyclopropyl radical.[9]

In its relative reactivity toward toluene, ethylbenzene and cumene the more highly substituted 1-methyl-2,2-diphenylcyclopropyl radical,[12] derived from the decomposition of the precursor diacyl peroxide, resembles the chlorine radical more than it does the phenyl radical (Table 3). Similarly, comparison of the relative reactivities of primary, secondary and tertiary aliphatic hydrogens toward chlorine atoms (1.0:3.6:4.2)[13] and phenyl radicals (1.0:9.3:44)[13] with the relative reactivities of the methanol/ethanol/2-propanol series toward the 1-methyl-2,2-diphenylcyclopropyl radical (1.0:2.4:3.5)[12] further confirms the low selectivity of the cyclopropyl radical. Again, this radical resembles the chlorine atom in its reactivity more than it does the phenyl radical.

Table 2. Relative reactivity in homolytic aromatic substitution

Aromatic			
C_6H_5Cl	3.5	1.1	1.78
$C_6H_5OCH_3$	2.3	1.7	1.95
C_6H_5CN	27	3.7	3.59
$C_6H_5CH_3$	0.76	1.2	1.03
$C_6H_5Bu(t)$	0.28	0.64	0.59

Table 3. Relative reactivities (per hydrogen) of hydrogen donors toward a variety of radicals

Hydrogen	Bromine atom 40°	Methyl 65°	Phenyl 60°	Chlorine atom 40°	1-Methyl-2,2-diphenylcyclopropyl 65°
Toluene	1	1	1	1	1
Ethylbenzene	17.2	4.1	4.6	2.5	1.8
Cumene	37.0	12.9	9.7	5.5	2.5

In so far as the rate of formation of radicals reflects their stability or reactivity the findings of Hart[14] are instructive. In carbon tetrachloride the rate of decomposition of benzoyl peroxide was twice as fast as that of biscyclopropanoyl peroxide. Other findings which show the difficulty in forming the cyclopropyl radical are seen in the failure of chlorine atoms to abstract the tertiary ring hydrogen from methylcyclopropane[15] and the failure of t-butoxy radicals[16] to abstract the tertiary hydrogen from a variety of alkylcyclopropanes. Hydrogen abstraction from the cyclopropylcarbinyl C atom is, as expected, preferred in these cases. The failure of cyclopropanecarboxyaldehyde to undergo decarbonylation reaction with di-t-butyl peroxide[17] to yield the cyclopropyl radical is another good example of the difficulty in producing the cyclopropyl radical. However, 1-methyl and 1-phenylcyclopropane carboxyaldehyde did decarbonylate to yield methyl and phenylcyclopropane, respectively. Also, photochemical chlorination[18] and vapor phase nitration[19] of cyclopropane have been reported. The relative reactivity of cyclopropane vs neopentane toward a variety of radicals is shown in Table 4.

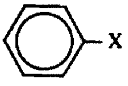
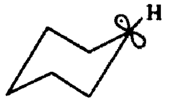
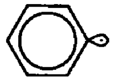
Table 4. Relative reactivities of C–H bonds, cyclopropane: neopentane toward radicals

Radical	T°C	Rel. Reactivity
$Cl\cdot_{(g)}$	250	0.03
$Cl\cdot_{(l)}$	68	0.13
$CH_3\cdot$	182	0.65
CH_3O	250	0.4
t-BuO·	68	0.2

Of the cycloalkyl radicals, the cyclopropyl radical is the least nucleophilic. This is in keeping with the σ character of cyclopropyl radicals. Table 5 compares the *meta/para* ratios obtained from the reaction of phenyl σ radicals, cyclopropyl σ radicals and cyclohexyl π radicals with substituted benzene.[9]

Cyclopropylation and phenylation give a lower *meta/para* ratio than cyclohexylation for electron releasing *ortho/para* directing substituents and a higher one for electron withdrawing *m*-substituents.

Table 5. The *meta/para* ratios in radical aromatic substitution

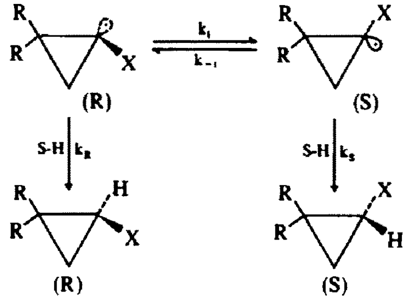
			
Cl	2.8	1.9	1.8
OCH_3	5.6	1.5	1.4
CN	0.09	0.43	0.33
t-Bu	2.5	1.9	1.8

This demonstrates that cyclopropyl and phenyl σ radicals are less nucleophilic than the cyclohexyl π radical. It has also been shown in radical substitution at the 2-position of a series of 4-substituted (CN, CH_3O, CH_3) protonated pyridines, that the cyclopropyl radical is the least nucleophilic of the cycloalkyl radicals.[20] This low nucleophilicity is consistent with the observed difficulty[21] in oxidizing the cyclopropyl radical by Cu^{2+}.

In summary, the cyclopropyl radical behaves as a rapidly inverting σ radical of high reactivity (low selectivity) and low nucleophilicity.

STEREOCHEMISTRY

If the cyclopropyl radical is a rapidly inverting σ radical ($10^8 s^{-1}$) is there any possibility that such a radical, generated at a chiral center, could maintain its configuration? Obviously for this to happen the radical would have to react, i.e. abstract an hydrogen atom faster than it inverts. Since the inversion frequency ($\sim 10^8 s^{-1}$) is close to that of the diffusion rate ($\sim 10^{10} s^{-1}$) a reaction in which the configuration is maintained must occur at a rate faster than the diffusion of the radical through the solvent. The only hope of observing a chiral radical is either to slow down the inversion frequency (k_i) and/or increase the rate of reaction (k_R, k_S). The former might be accomplished by introducing a substituent X which is capable of decreasing the inversion frequency (k_i) or by placing the radical on a solid surface with which it can somehow interact. A cage reaction, disproportionation or combination, would also lead to retention of configuration since k_R might be expected to be very much greater than k_i.



Effect of substituent X

Theoretical considerations. In general, increasing the s-character of the orbital containing the unpaired electron will stabilize the σ radical and decrease the rate of inversion.[6] Both cyclopropyl and vinyl radicals are bent σ-radicals and their inversion barriers are larger than those of their acyclic and saturated counterparts.[22a]

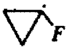
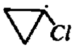
Two theories have been advanced to explain why electronegative substituents tend to cause the radical to be a σ radical. Pauling and Walsh[23] propose that the effect is due to a difference in electronegativity which would cause the orbital occupied by the odd electron to have a greater amount of s character and hence tend to be pyramidal. Any highly electronegative substituent would therefore enhance the non-planarity of the radical and the substituent effect should parallel the electronegativities of the group. Wells[24] has published a critical review dealing with group electronegativities; a portion of his compilation of mutually consistent group electronegativities is presented in Table 6.

Table 6. Mutually consistent group electronegatives

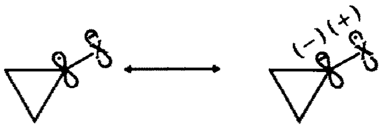
Group	Empirical values	Group	Empirical values
F	3.95	Cl	3.03
CH_3O	3.70	Br	2.80
H_2N	3.35	CH_3	2.30
CF_3	3.35	H	2.28

Dewar[22b] argues that the electronegativity of the substituent is not the factor which accounts for the increased configurational stability of the free radicals and that stabilization in the cyclopropyl radical is due to an antibonding interaction between the nonbonding electrons of the substituent and the MO's arising from the interactions between the singly occupied carbon AO and the MO's of the adjacent C bonds. As the result of MINDO/3 calculations it was predicted that the barrier to inversion, caused by a substituent at the radical site, should increase in the order O < Cl < F. This order is at variance with that predicted solely on the basis of group electronegativities which would be Cl < OCH_3 < F. CNDO/2 calculations[25] of inversion barriers of a number of α-substituted cyclopropyl radicals are given in Table 7.

Table 7. CNDO/2 calculations[25]

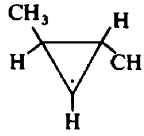
Radical			
Inversion Barrier (kcal/mole)	10.5	4.0	0.8

Electronegativity may be a necessary but not a sufficient property to cause a radical to maintain its configuration. As we can see from Table 6 the CF_3 group is highly electronegative yet the geometry of a carbon radical to which it is attached is not much affected by replacing the hydrogens with CF_3 groups.[26] Another important factor is whether or not there is a significant delocalization in the transition state for the inversion process when the σ radical becomes a π radical. When this type of delocalization becomes significant then the energy barrier for inversion will be lowered. With second row elements such as N,O and F, contributions from this type of delocalization will be minimal. They will only become significant for higher row elements, i.e. S, Cl, Br, and I or when X is part of a π system such as a carbon in a vinyl, cyano, carbonyl, etc.

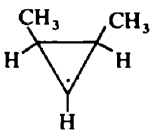


Fluorine. As the most electronegative element, fluorine would be expected to have the greatest effect on the stereochemical stability of the cyclopropyl radical and it does. When comparing esr spectra of cyclopropyl radicals (X = H) and the 1-fluoro analogues Kawamura[27] found the inversion frequencies at −99° of **1**, **2** and **3** to be comparable to that found for the cyclopropyl radical itself,

$\sim 10^8 s^{-1}$. In contrast, the inversion frequency of the α-fluorocyclopropyl radical **4**, **5** and **6** is estimated to be lowered to $\sim 10^6 s^{-1}$ at $-108°$.



1



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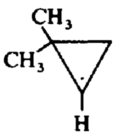

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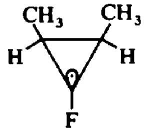

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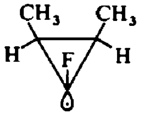

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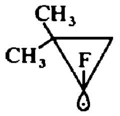
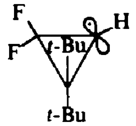
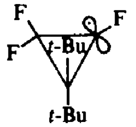


6

Steric effects also play a role in determining whether a cyclopropyl radical will be a rapidly inverting σ radical or a π radical. Ingold[28] has concluded from an analysis of the ESR spectra of **7** and **8** that although the radical **3** is a σ radical having a pyramidal structure, **7** is a planar π radical. Moreover, **8** is also a planar or near planar π radical whereas **3** is an inverting bent σ radical. The unusual configuration of **7** and **8** is believed to be due to steric repulsion between the t-butyl groups and the α-hydrogen or α-fluorine.

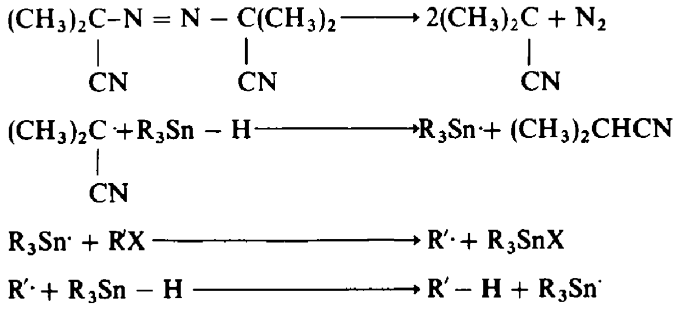


7



8

Can an α-fluorine substituent reduce the inversion frequency (k_i) of the inverting cyclopropyl σ radical sufficiently so that it can maintain its stereochemistry in a chemical reaction? The answer is yes, when an efficient radical trap is available so that $k_{(R)} \gg k_i$ (Scheme 1). The tin hydrides provide such an efficient radical scavenger[29] as well as the means to generate radical intermediates by their reaction with alkyl halides.[30] The reaction usually involves the use of a radical initiator such as azobisisobutyronitrile (AIBN) or di-t-butyl peroxide (DTBP). The reaction mechanism is depicted in Scheme 2.



$$\underset{\mathrm{CN}}{(CH_3)_2C}-N=N-\underset{\mathrm{CN}}{C(CH_3)_2} \longrightarrow 2\underset{\mathrm{CN}}{(CH_3)_2C} + N_2$$

$$\underset{\mathrm{CN}}{(CH_3)_2C}\cdot + R_3Sn-H \longrightarrow R_3Sn\cdot + (CH_3)_2CHCN$$

$$R_3Sn\cdot + R'X \longrightarrow R'\cdot + R_3SnX$$

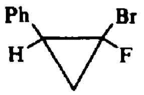
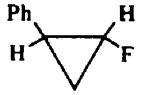
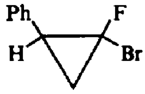
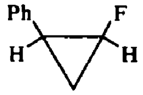
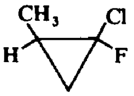
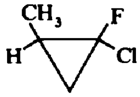
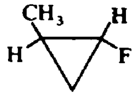
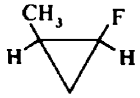
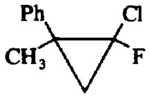
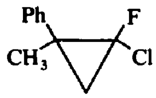
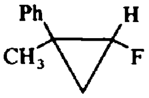
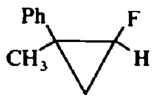
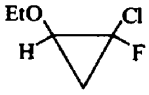
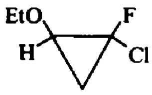
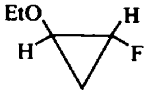
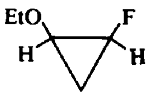
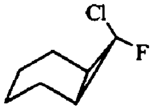
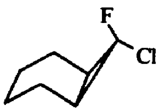
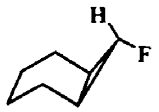
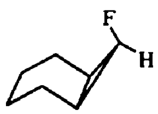
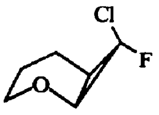
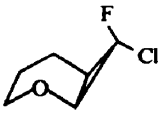
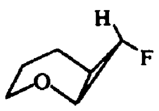
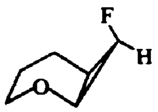
$$R'\cdot + R_3Sn-H \longrightarrow R'-H + R_3Sn\cdot$$

Scheme 2.

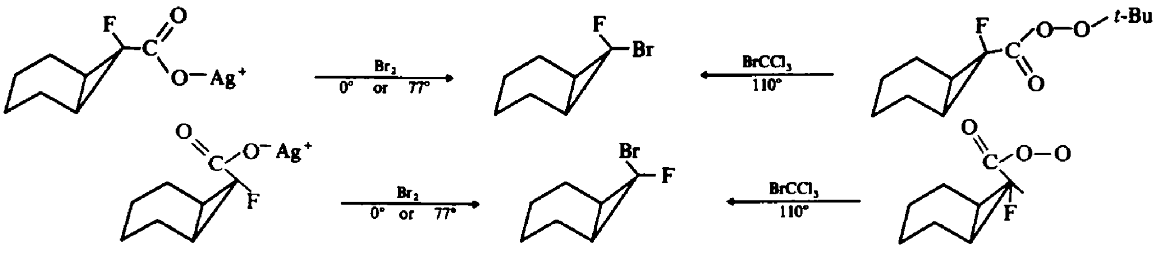
Ando *et al.*[31] reduced a series of *gem*-halofluorocyclopropanes with tri-n-butyltin hydride to yield the corresponding monofluorocyclopropanes. Table 8 lists a number of representative *gem*-fluorochlorocyclopropanes that have been reduced. The results are striking in that the reactions are completely stereospecific under the conditions specified. The effect of the α-fluoro substituent in slowing down the inversion frequency (k_i) of the σ radical combined with the propensity of the tin hydride to react with the radical[29] (k_R) best accounts for these observations.

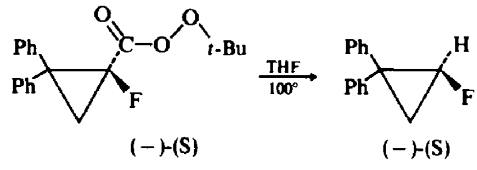
Kaplan[32] has compared the hydrogen-transfer ability of various Group IV hydrides toward radicals and found the order (k_R) $R_3Sn\text{-}H > R_3\text{-}Ge\text{-}H > R_2Si\text{-}H_2 > R_3Si\text{-}H$. Yamanaka[33] has shown that the same order is followed in the reduction of 1-bromo-1-fluoro-2-phenylcyclopropane. Whereas using tri-n-butyltin hydride gives stereospecific reduction, the use of

Table 8. Stereochemistry of reduction of *gem*-halofluorocyclopropane with tri-n-butyltin hydride.[31]

Run	Isomer(s) Reduced	Isomer ratio	Temp.°C	Product(s)	Isomer ratio
1		100:0	135		100:0
2		100:0	135		100:0
3	 : 	66:34	90	 : 	67:33
4	 : 	52.48	135	 : 	53:47
5	 : 	60:40	85	 : 	61:39
6	 : 	58:42	90	 : 	58:42
7	 	61:39	80	 	65:35

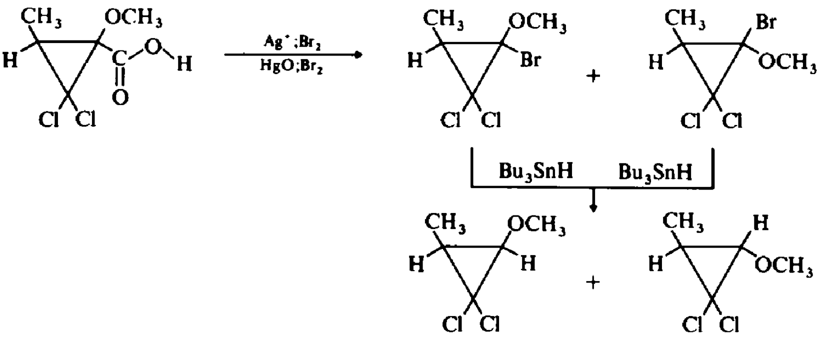
di-n-butylsilicon dihydride gave slightly less retention (97%) and with tri-n-butylsilicon hydride the retention was reduced to 84%. Ando and Yamanaka[34] have also demonstrated that the brominative decarboxylation (Hunsdiecker reaction) of an α-fluorocyclopropanecarboxylic acid proceeds in a stereospecific manner, this again reflects the ability of an α-fluorine substituent to stabilize the configuration of a cyclopropyl radical and suggests that the bromine radical is also an efficient radical trap. Moreover, they have shown that the thermal decomposition of *exo* and *endo* t-butyl 7-fluoronorcarane-7-peroxycarboxylates in $BrCCl_3$ produced the corresponding 7-bromo-7-chloronorcarane with 100% retention of configuration. Replacing $BrCCl_3$ as a solvent by a poorer radical trap solvent, such as toluene and cumene, reduced the stereospecificity by only 6–10%. Walborsky and Collins[35] showed that thermal decomposition of t-butyl (−)-(S)-1-fluoro-2,2-diphenylcyclopropanepercarboxylate in tetrahydrofuran, a markedly inferior radical scavenger solvent, resulted in the formation of (−)-(S)-1-fluoro-2,2-diphenylcyclopropane of overall retained configuration but only 47% optical purity or 74% retention of configuration.



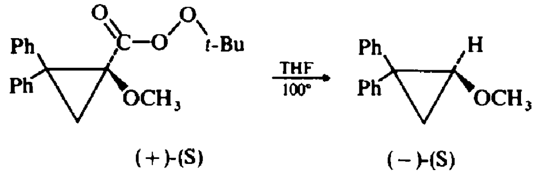


In summary, the α-fluoro substituent on a cyclopropyl radical has a marked effect on the ability of the radical to maintain its configuration. For reasons previously discussed, the strongly electronegative atom decreases the inversion frequency (k_i) of the cyclopropyl σ radical; the electronegative atom decreases the inversion frequency (k_i) of the cyclopropyl σ radical; this combined with a good radical scavenger makes $k_R \gg k_i$ (Scheme 1) and results in a high retention of configuration.

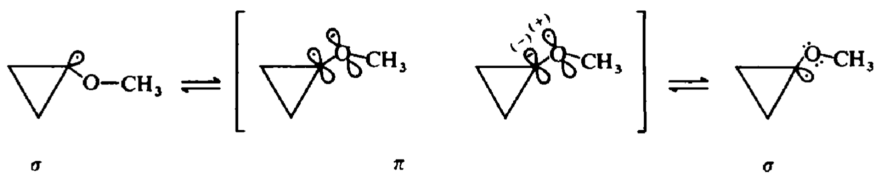
Methoxyl. An α-methoxyl group would also be expected to stabilize the configuration of the cyclopropyl radical since oxygen is an electronegative atom. There have been two investigations of the methoxyl group as a substituent, Ando and Yamanaka[36] reported on the Hunsdiecker reaction of *trans*-1-methoxy-2-methyl-3,3-dichlorocyclopropanecarboxylic acid. At 0° use of either the silver salt or the Cristol-Firth method (HgO) and bromine yielded a ~57:43 mixture of isomers with overall retention of configuration. However, at 77° a ~39:61 ratio of isomers was produced indicating overall inversion of configuration. Unfortunately, decomposition of the *cis*-1-methoxy-2-methyl-3,3-dichlorocyclopropanecarboxylic acid was not studied to ascertain whether the product ratios represented a thermodynamic or kinetically controlled reaction. That the reaction is probably thermodynamically controlled was indicated by tri-n-butylin hydride reduction of each of the isomers resulting from the Hunsdiecker reaction. Both isomers at 0° gave approximately the same ratio (~54:46) of products.



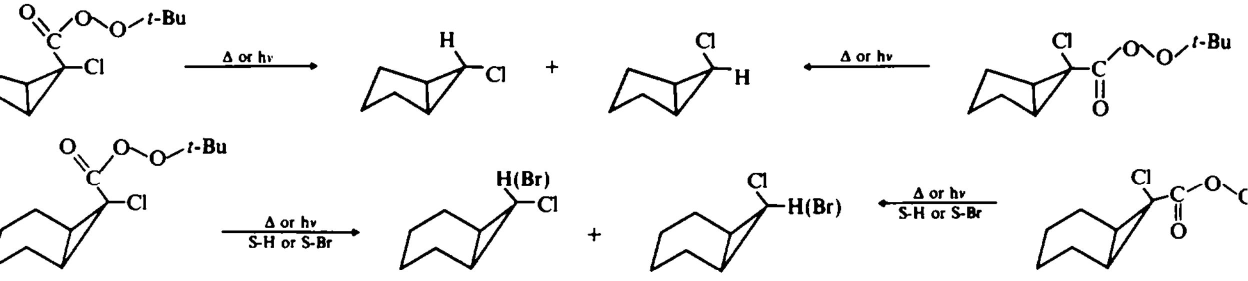
Walborsky and Collins[35] decomposed chiral t-butyl (−)-(S)-1-methoxy-2,2-diphenylcyclopropanepercarboxylate in tetrahydrofuran and isolated, *inter alia*, (+)-(S)-1-methoxy-2,2-diphenylcyclopropane with an optical purity of 8% or an overall retention of configuration of 54%.

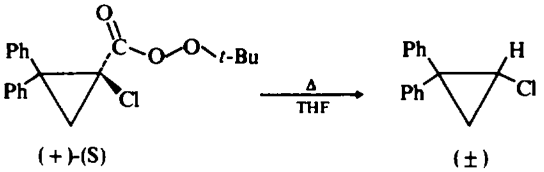


The results of these limited experiments suggest than an α-methoxyl group is not very effective in stabilizing the configuration of the cyclopropyl radical[38] and indicates that delocalization of the radical by the methoxyl group may be making an important contribution to the stabilization of the π radical intermediate or transition state.

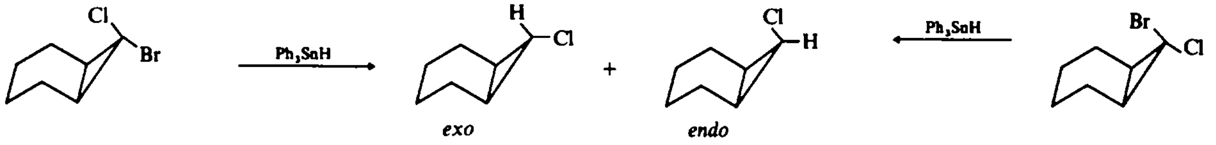


Chlorine. Singer and Chen[39] demonstrated the inability of an α-chlorine substituent to stabilize the configuration a cyclopropyl radical. They showed that thermal and photochemical decomposition of both *exo* and *endo* t-butyl 6-chlorobicyclo[3.1.0]hexane-6-percarboxylate in toluene or diisopropylbenzene resulted in an identical mixture of *exo* and *endo* 6-chlorobicyclo[3.1.0]hexane. A similar result[34] was obtained in the thermal decomposition of both *exo* and *endo* t-butyl-7-chlorobicyclo[4.1.0]heptane-7-percarboxylate. In solvents such as toluene, cumene or bromotrichloromethane the same ratio (80:20) of *exo* and *endo* products was formed within experimental error. These observations are supported by our own findings that the thermal decomposition of t-butyl (+)-(S)-1-chloro-2,2-diphenylcyclopropanepercarboxylate in tetrahydrofuran resulted in completely racemic 1-chloro-2,3-diphenylcyclopropane.[35] Surprisingly, the Hunsdiecker reaction using the silver salts of *exo* and *endo* 7-chlorobicyclo[4.1.0]heptanecarboxylic acids and bromine at 0° did not result in the same ratio of products but instead showed a high retention to inversion ratio of 88:12 for the *exo* acid and 82:18 for the *endo* acid.[34] This anomolous result may be a reflection of the bromine radicals ability to trap the cyclopropyl radical but, this is unlikely. Altman[25] found that the reduction of each of the isomers of 7-bromo-7-chlorobicyclo[4.1.0]heptane by the excellent radical scavenger triphenyltin hydride resulted in an identical mixture (79:21) of *exo* and *endo* 7-chlorobicyclo[4.1.0]heptane. This ratio of products is, within experimental error, identical with that found in the thermal decomposition of *exo* and *endo* t-butyl 7-chlorobicyclo[4.1.0]heptane-7-percarboxylate[34] in cumene.





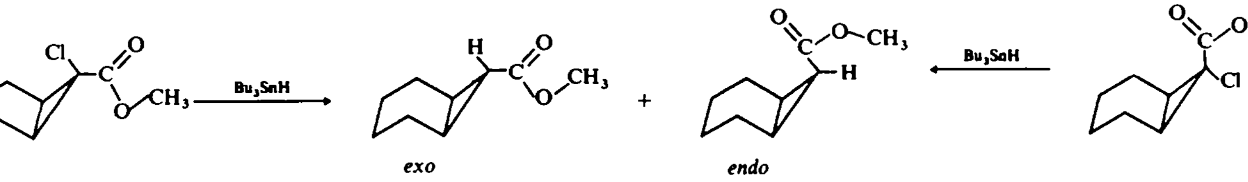
(+)-(S) (±)



exo *endo*

The available evidence points to the conclusion that an α-chloro substituent on a cyclopropyl radical does not help to maintain the configuration of the cyclopropyl radical. The radical is either a rapidly inverting σ radical or a π radical if the chlorine substituent is delocalizing the radical through the use of its empty d orbitals.

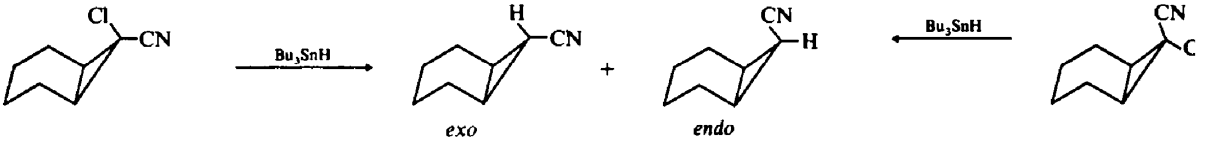
Carbomethoxyl and cyano. As expected delocalizing substituents such as carbomethoxyl and cyano should decrease the barrier to inversion and perhaps may even convert the rapidly inverting σ radical to a linear π radical. The net result should be a loss of configuration. Ando and coworkers[40] have shown this to be the case in the tri-*n*-butyltin hydride reduction of the isomeric *exo* and *endo* 7-



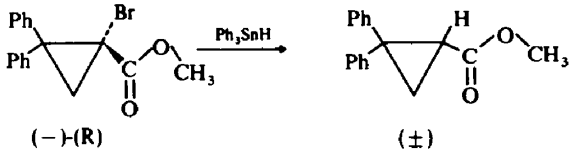
exo *endo*

chloro-7-carbomethoxybicyclo[4.1.0]heptane. Both isomers gave the same ratio of *exo* and *endo* (7:93) methyl bicyclo[4.1.0]heptane-7-carboxylate.

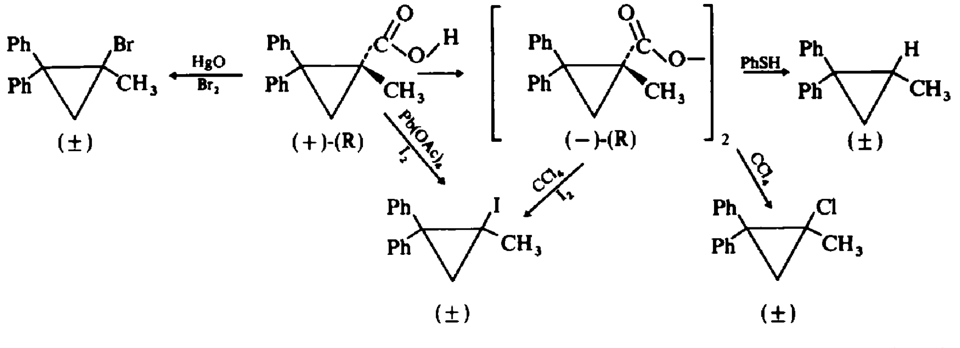
A similar result was obtained in the reduction of each of the isomeric *exo* and *endo* 7-chloro-7-cyanobicyclo[4.1.0]heptanes. Both isomers gave the same ratio of *exo* and *endo* (6:92) 7-cyanobicyclo[4.1.0]heptane.



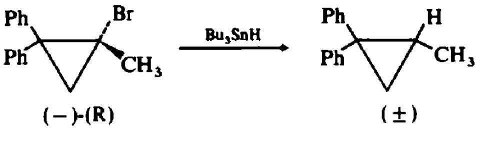
The triphenyltin hydride reduction of methyl (−)-(*R*)-1-bromo-2,2-diphenylcyclopropylcarboxylate resulted in essentially racemic methyl 2,2-diphenylcyclopropylcarboxylate.[41]



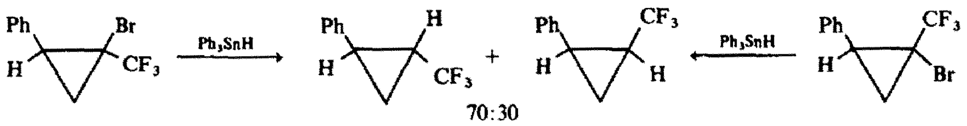
Methyl and trifluoromethyl. The accumulated evidence indicates that an α-methyl substituent attached to the cyclopropyl radical has very little, if any, effect in helping to maintain the configuration of the radical. We have shown[42,43] that thermal decomposition of the diacyl peroxide of (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid in THF yielded, *inter alia*, the hydrocarbon 1-methyl-2,2-diphenylcyclopropane which was essentially racemic. Moreover, thermolysis in carbon tetrachloride produced racemic 1-chloro-1-methyl-2,2-diphenylcyclopropane and even the addition of a good radical trap such as iodine produced only racemic 1-iodo-1-methyl-2,2-diphenylcyclopropane. The latter reaction presumably involves the formation of an intermediate hypoiodite which decomposes to the iodide by a radical pathway. Other reactions, which presumably involve similar intermediates, are the lead tetracetate-iodine procedure for the decarboxylation of carboxylic acids[44] and the Cristol-Firth[45] reaction (HgO/Br_2 in CCl_4). Both of these reactions yield the corresponding racemic iodide and bromide.[42,43]



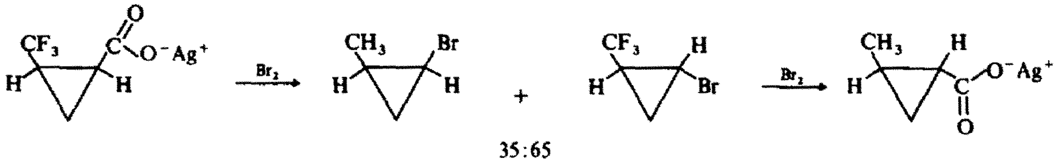
Further attempts to trap the 1-methyl-2,2-diphenylcyclopropyl radical, before inversion, by using excellent radical scavengers as solvents were also abortive. Decomposition of the diacyl peroxide in thiophenol and reduction (−)-(*R*)-1-bromo-1-methyl-2,2-diphenyl cyclopropane with tri-n-butyltin hydride as solvent resulted in essentially racemic hydrocarbon.[42,43]

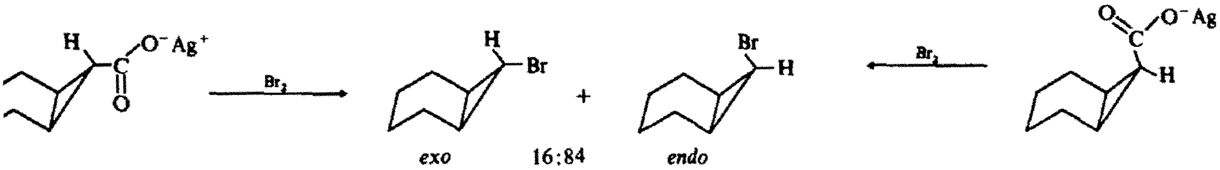


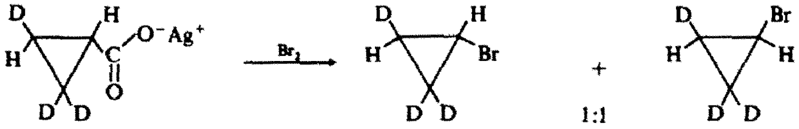
As was discussed earlier, although the CF_3 group is an electronegative substituent its influence on stabilizing the configuration of a cyclopropyl radical is similar to that of a methyl group rather than a fluorine group.[26] Thus, Altman[46] has shown that the reduction of *cis* and *trans*-1-bromo-1-trifluoromethyl-2-phenylcyclopropane with a large excess of neat triphenyltin hydride gives complete configurational equilibration of the radical.



Hydrogen. Hunsdiecker reaction of both *cis* and *trans*-2-methylcyclopropanecarboxylic acid yielded the same mixture (35:65) of *cis* and *trans*-1-bromo-2-methylcyclopropane, thus demonstrating that the 2-methylcyclopropyl radical was incapable of maintaining its configuration.[47a] Brominative decarboxylation of *exo* and *endo* norcarane-7-carboxylic acid produced the same mixture (16:84) of *exo* and *endo* 7-bromo-norcarane.[34] Consistent with these results is the recent report that the Hunsdiecker reaction with *trans*-2,2,3-d_3-cyclopropanecarboxylic acid gives an equimolar mixture of *cis* and *trans*-1-bromo-2,2,3-d_3-cyclopropane.[47b]



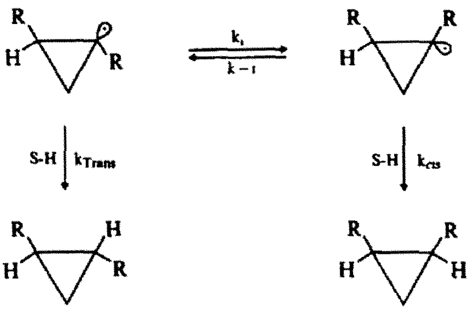




In summary, it can be stated that both the 2° cyclopropyl radical (α-H) and the 3° cyclopropyl radical (α-CH_3) are rapidly inverting σ radicals incapable of maintaining their configurations.

REGIOSELECTIVITY OF THE RAPIDLY INVERTING σ RADICAL

In those cases where the inversion rate (k_i) of the σ radical is faster than the trapping of the radical ($k_{cis/trans}$) the product of the reaction will reflect the thermodynamic stability of the radical assuming that $k_{trans} = k_{cis}$. This assumption is not necessary when the reaction is analyzed by ESR since one is



observing the radical directly. Table 9 lists the structures of the thermodynamically more stable cyclopropyl radicals. There are a number of factors which will influence the position of the equilibrium. Among them are steric effects and electronic effects. As can be seen in Table 9 entries **4, 5** and **11–19** are examples in which the position of the equilibrium is influenced by steric interactions. Entry **4** shows that the σ orbital containing the odd electron prefers to be *cis* to the phenyl group to avoid the more sterically hindered situation which would place the CF_3 and phenyl group *cis* to each other. In bicyclo[1.1.0]butane (entry **6**) severe hydrogen-hydrogen interaction is relieved by having the σ orbital which contains the odd electron in the endo position. A similar situation obtains in entries **18** and **19**. Entry **11** illustrates the result of steric interaction between an *endo* substituent on C-

Table 9. Structures of the thermodynamically favored σ radical

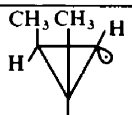
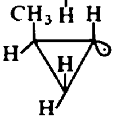
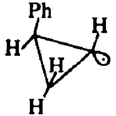
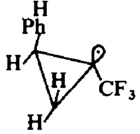
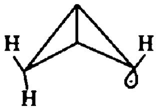
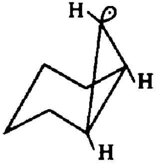
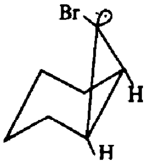
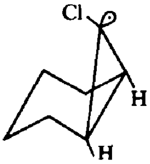
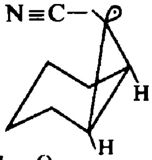
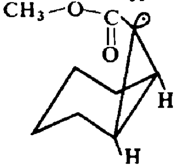
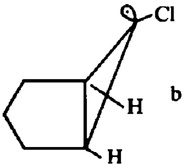
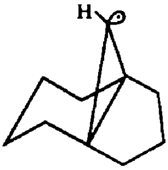
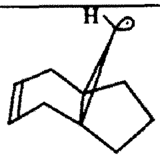
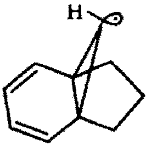
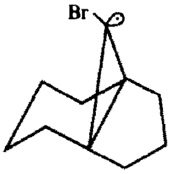
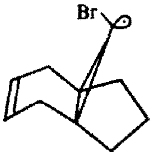
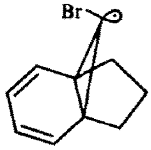
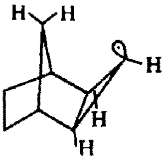
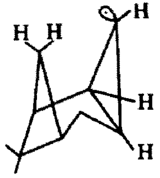
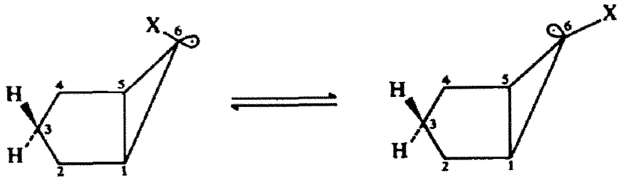
Entry	Structure	% at Equilib.	Method(c)	References
1		92	c-3,c-4	49,27
2		65	c-1	47
3		79	c-3	49
4		70	c-2	47
5		mainly	c-4	27
6		~84	c-1	34
7		75-80	c-1,c-2	33
8		80	c-2,c-5	25,34
9	 a	92	c-2	40
10	 a	94	c-2	40
11	 b	67	c-5	39
12		94-100	c-2	48

Table 9—contd.

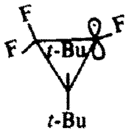
Entry	Structure	% at Equilib.	Method(d)	References
13		94-100	c-2	48
14		95	c-2	48
15		80	c-2	48
16		77	c-2	48
17		87	c-2	48
18		70	c-3,c-4	70,27
19		100	c-2	51

(a) This radical may well be a π radical rather than a σ radical.
(b) Result in toluene; opposite result obtained in diisopropylbenzene
(c) Only one isomer used to generate radical.
(d) c-1 (Hunsdiecker): c-2 (tin hydride): c-3 (dissolving metal): c-4 (esr): c-5 (acyl peroxide).

6 and the *endo* hydrogen on C-3. This *endo–endo* interaction is relieved when the C-6 σ radical orbital occupies the *endo* position. This same type of interaction would account for the results observed with the radicals shown in entries **11–17**. Steric interactions not only play an important role in determining the regioselectivity of the radical but, when severe, can even cause a σ radical to be converted to a π-radical. This was demonstrated by Ingold[28] in the case of the 1,2,2-trifluoro-3,3-di-t-butylcyclopropyl radical. Ordinarily the α-fluoro radical would be a σ radical but due to the steric effects of the bulky t-butyl groups it has been converted to a π radical.



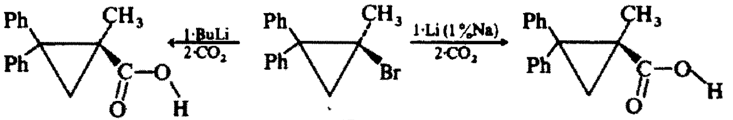
One could interpret the results of entries **1–3** and **6–10** as being due to electronic effects. Dewar[52] has suggested that there is a stabilizing interaction between the orbital containing the odd electron and *cis* hydrogen substituents on adjacent β-carbon atoms. This suggestion is reinforced by esr observations that there is a larger hfsc with the *cis* β-hydrogens than with the *trans* ones.[27] Such a stabilizing effect would account for the results observed (**1–3** and **6–10**).



The steric and electronic arguments are not all that clear cut. Without esr evidence to the contrary one might interpret the results in entries **1–3** and **6–10** as being due to the radical being either a π radical (**7–10**) or rapidly inverting σ radical and that the regioselectivity observed is due to a difference in k_{cis} and k_{trans} caused by the approach of S–H from the least hindered side of the radical. At the current state of knowledge this interpretation is a viable one for these molecules but can certainly be excluded for entries **5**, **11**, **18**, **19** and possibly **13–19**.

CYCLOPROPYL RADICALS AT METAL SURFACES

(a) *Lithium surface.* The stereochemical results of σ radicals generated in solution and at metal surfaces can vary greatly. For example, genesis of the 1-methyl-2,2-diphenylcyclopropyl σ radical in solution, by decomposing its chiral diacyl peroxide precursor leads to formation of completely racemic product. This is so even when good radical traps such as iodine or thiophenol are present[42,43] (*vide supra*). By contrast reaction of chiral (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane with lithium metal followed by carbonation leads to the formation of (−)-(S)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid with 73% retention of configuration[53] (45% optical purity). It was shown that the loss of configuration was not due to racemization of the lithium reagent, once formed in solution, since preparation of the same lithium reagent by halogen-lithium exchange of the bromide with butyllithium produced, after carbonation, the acid with 100% retention of configuration. Halogen-lithium exchange was shown to proceed with complete retention of configuration and the 1-methyl-2,2-diphenylcyclopropyllithium produced in this manner was shown to be configurationally stable at ambient temperatures and over extended periods of time.[54]



(−)-(S)
100%

(−)-(S)

(+)-(S)
73%

The nature of the lithium surface is important. Varying the particle size of the lithium dispersion from 25μ with a surface area of 2782cm^2 to 150μ with a surface area of 464cm^2 reduced the optical purity of the resulting acid by nearly 50%. It was also demonstrated that the amount of sodium impurity in the lithium dispersion had a significant effect not only on the stereochemical results of the metallation reaction but also on the reactivity of the metal surface itself. For example, reaction of chiral 1-iodo-2,2-diphenylcyclopropane with 25μ lithium dispersions containing 0.002%, 0.02% and 1% sodium yielded after carbonation 1-methyl-2,2-cyclopropanecarboxylic acid with optical purities of 13%, 16% and 36% respectively. The increase in optical purity with increase in sodium content may be a consequence of lowering the ionization potential of the metallic surface.[55]

Table 10. Lithiation of chiral 1-Halo-1-methyl-2,2-diphenylcyclopropane followed by carbonation

Halide	Temp.(°C)	Time (min)	Acid Yield, %	Optical Purity, %
Cl	25	40	73	63
Br	26	42	70	45
I	25	41	60	36

The stereochemistry of the reaction is also dependent on the halogen. The reaction of chiral 1-halo-2,2-diphenylcyclopropane with 25μ lithium dispersions containing 1% sodium produced the results shown in Table 10. It should be noted that the optical purity of the acid varies in the same order as the carbon halogen bond strength Cl > Br > I.

The following mechanism[53] was proposed by us in 1965 for the lithiation reaction (Fig. 2). The stereochemistry of the reaction may be explained by a single electron transfer (SET) to the carbon-halogen bond which results in either the formation of a radical anion on the metal surface (**1**) or what is in essence a loose radical pair (**2**). The radical anion can collapse (**4**) to form lithium reagent with retention of configuration or dissociate (**3**) to the loose radical pair. The radical (R) in the loose radical pair can undergo rotation before the next SET occurs and this would yield the racemic lithium reagent. As the halogen (X) is changed from iodide to bromide to chloride the bond energy increases and reaction pathways (**1**) and (**4**) are favored and results in a decrease in the amount of loose radical pair formation. Moreover, increasing the surface area and/or decreasing the ionization potential (increased sodium content) would also favor pathways (**1**) and (**4**) resulting in an increase of retention of configuration.

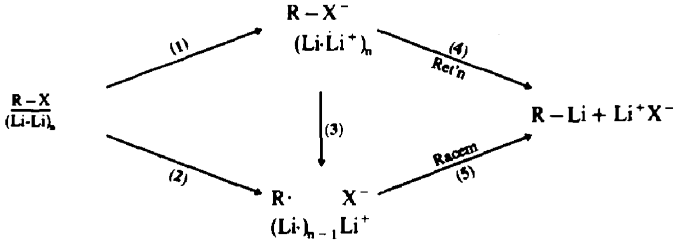
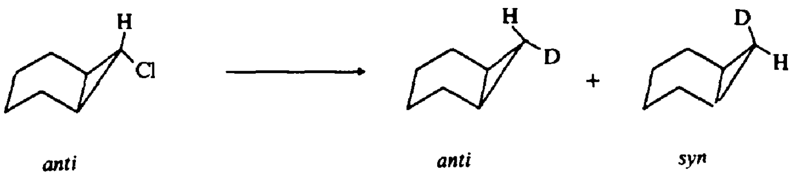


Fig. 2. A mechanistic scheme for the formation of lithium reagents.

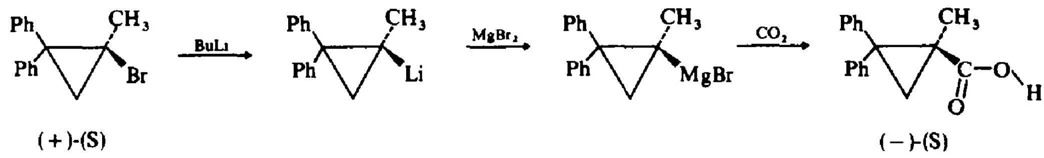
In solution the 1-methyl-2,2-diphenylcyclopropyl σ radical racemizes[42,43] but when the radical is formed at the surface *via* intermediate ion radical precursors, the overall result is a retention of configuration. It may therefore be dangerous to draw conclusions about the stereochemical fate of σ radicals under these conditions.[56] For example, *cis* and *trans*-1-bromo-2-methylcyclopropane when treated with metallic lithium yield products with 8–38% retained configuration.[57] In one interpretation[57] it was claimed that the observed retention of configuration is due to the intrinsic stability of the intermediate σ cyclopropyl radical. More likely, the retention is due to a surface effect as described above since it has previously shown that Hunsdiecker reaction with both *cis* and *trans*-2-methylcyclopropanecarboxylic gave identical mixtures of products[47] thus demonstrating that the 2-methylcyclopropyl radical is incapable of maintaining its configuration in solution.

The effect of surface has also been demonstrated in the reduction of *anti*-3-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane.[50] When the reduction is carried out by lithiation in ether followed by deuterolysis the ratio of *syn* product to *anti* product was about 2:1 whereas reduction under homogeneous conditions, lithium naphthalenide followed by deuterolysis, resulted in a 30:1 ratio. Again, greater retention on the metal surface. The *syn* σ radical was shown to be the thermodynamically more stable (Table 8).



(b) *Magnesium surface*. In 1961 we observed that the reaction of chiral 1-bromo-1-methyl-2,2-diphenylcyclopropane with magnesium metal produced a partially optically active Grignard reagent.[58] It was suggested that the racemization observed occurred in the Grignard formation step. In 1964 we published[59] our results which proved that the racemization occurred at some stage preceeding Grignard formation by showing that once the Grignard reagent was formed it was optically stable. This was accomplished by preparing the Grignard reagent from the optically stable lithium reagent[54] by treatment with anhydrous magnesium bromide followed by carbonation. The acid produced in this manner was optically pure.

There is no doubt that the 1-methyl-2,2-diphenylcyclopropyl σ radical is incapable of maintaining its configuration when it is formed in solution.[42,43] How can one account for the retention of



configuration and optical activity that is observed? In 1964 we proposed (Fig. 3), our mechanism of Grignard formation[59] which was elaborated[60] upon in 1973.

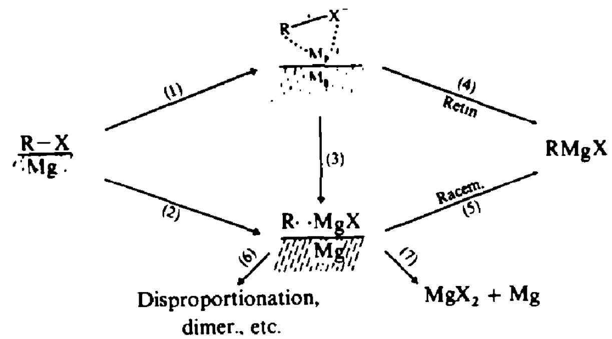
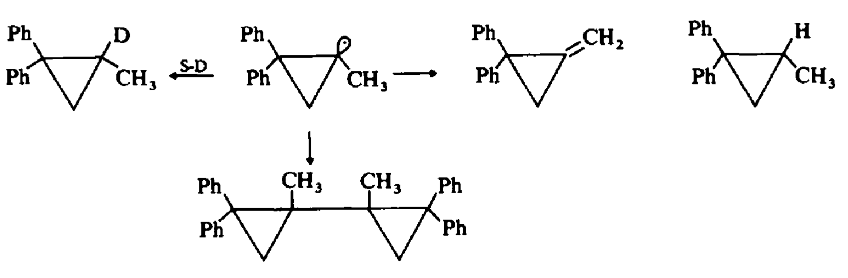


Fig. 3. A mechanistic scheme for Grignard reagent formation.

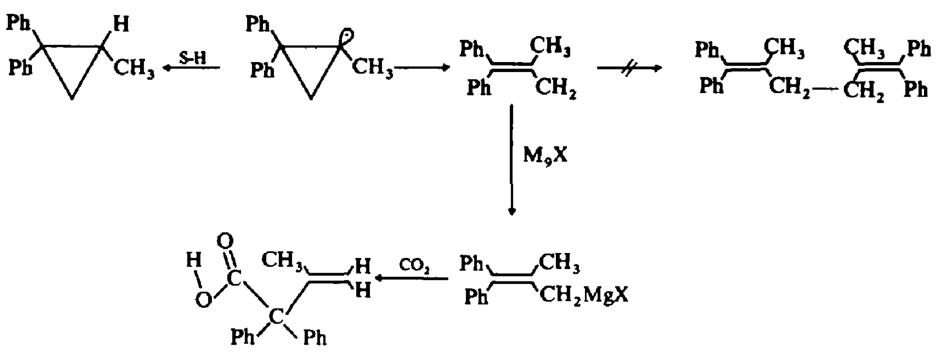
The processes pictured in Fig. 3 takes place at the magnesium-solution interface. Interaction of the cyclopropyl halide and magnesium by pathway (1) involves electron transfer from the metal into the antibonding carbon-halogen bond to give a radical anion in close association with a univalent magnesium cation. Collapse of the tight anion radical-cation radical pair, pathway (4), leads to Grignard reagent formation with complete retention of configuration. Alternatively collapse may proceed by pathway (3) to a loose radical pair which may also be formed directly by pathway (2). Bodewitz, Blomberg and Bickelhaupt[61] have recently provided CIDNP evidence for pathway (2). It is in the loose radical pair that racemization can take place. Combination of the cyclopropyl radical with the magnesious halide radical produces largely racemic Grignard reagent (pathway (5)). The kinetic analysis of Grignard formation by Whitesides *et al.*[62] is also consistent with pathway (1) and/or (2) being involved in the rate of determining step.

The σ cyclopropyl radical may, however, escape capture by the magnesious halide and undergo typical radical reactions of disproportionation and dimerization, pathway (6), all at the surface. Or some radicals may leave the surface and abstract a hydrogen atom from the solvent. Consistent with the surface nature of the reaction is the observation that very little ring opened product is observed.



When the radical is generated in ether solution by thermal decomposition of the diacyl peroxide, the products consist of the cyclopropyl hydrocarbon and a dimeric product resulting from ring opening.[42,43] The only ring opened product appears in the acid fraction, after carbonation of the Grignard solution. The allyl radical produced by the ring opening is captured by the magnesious halide. Further confirmation of the surface nature of Grignard formation is the observation that when THF-d_8 and diethyl ether-d_{10} were used as solvent only 28 % and 6 % deuterium, respectively, were found in the hydrocarbon fraction of the reaction.[60,63] Moreover, the yield of hydrocarbons from reaction in THF is only ~1.0–1.5 % whereas in diethyl ether the yield is ~20 %. This is in accord with the greater solvating power of THF.[63] Recent XPS analysis of the Grignard formation reaction is consistent with the surface nature of the reaction.[64]

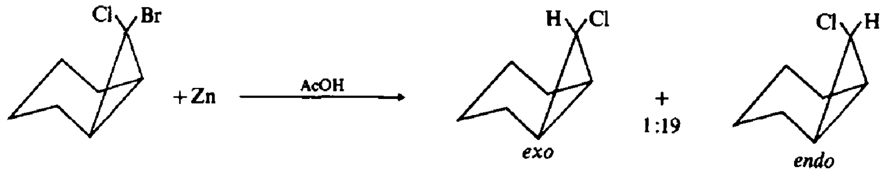
The effect of halogen (R–X) is evident in both the stereochemistry and the amount of Grignard reagent formed. The energy of the carbon-halogen bond increases in the order $I < Br < Cl$ as do the

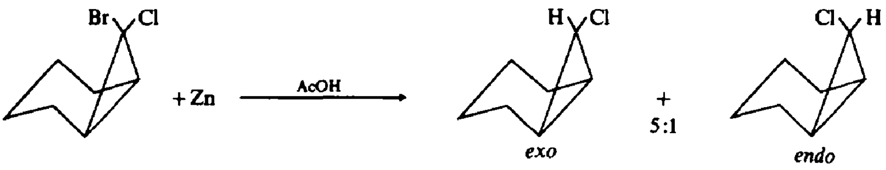


optical purities (2 %, 17 % and 26 % respectively) and yields of Grignard reagents (36 %, 70 % and 89 % respectively). This is consistent with the amount of loose radical pair formed, pathways (2) and (3), being determined by the strength of the carbon halogen bond,[63] i.e. the weaker the bond the greater the amount of loose radical pairs.

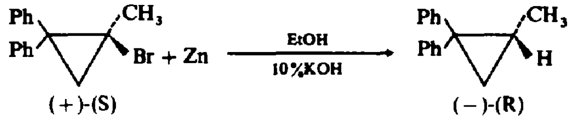
As with lithiation the retention of configuration and optical activity of the σ cyclopropyl radical is due to a surface interaction rather than to any intrinsic stability of the radical.

(c) *Zinc surface.* Triphenyltin hydride reduction[25] of either isomer of 7-bromo-7-chlorobicyclo[4.1.0]heptane resulted in an identical 1:4 mixture of *exo* and *endo*-7-chlorobicyclo[4.1.0]heptane. This same ratio was also obtained when *exo* and *endo* t-butyl 7-chlorobicyclo[4.1.0]heptane-7-percarboxylate was thermally decomposed in cumene.[34] As previously discussed the α-chlorocyclopropyl σ radical, generated *in solution*, is incapable of maintaining its configuration and the 1:4 *exo–endo* product ratio represents the thermodynamically controlled reaction mixture (Table 9). By contrast, the reaction of *exo*-7-bromo-*endo*-7-chlorobicyclo[4.1.0]heptane with zinc in an acetic acid-ethanol mixture yielded a mixture of *exo* and *endo*-7-chlorobicyclo[4.1.0]heptane with an *exo*:*endo* ratio of 1:19. This amounts to overall retention of configuration for the reduction and a ratio of products far from that expected for a thermodynamically controlled reaction. Moreover, the *endo*-7-bromo-*exo*-7-chloro isomer, under the same reaction conditions, gave an *exo*:*endo* ratio of 5:1 for the product mixture of *exo* and *endo*-7-chlorobicyclo[4.1.0]heptane. Again, an overall retention of configuration is observed with the thermodynamically less stable isomer predominating.[65]



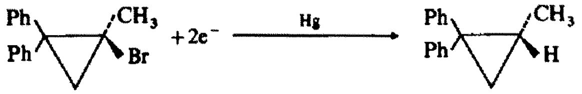


Erickson and Annino[65] have postulated a mechanism for the reaction at the zinc surface patterned after the one proposed by us for Grignard formation.[59,60] The organozinc intermediate formed is rapidly hydrolyzed by the protonic solvent. Note also that the reaction of zinc, in ethanol-10 % KOH, with chiral 1-bromo-1-methyl-2,2-diphenylcyclopropane yielded 1-methyl-2,2-diphenylcyclopropane with 21 % retention of configuration,[66] a result comparable to that found in Grignard formation (15 %).



(d) *Mercury surface.* As a first approximation one can view metallation and electrolytic reduction as a single class of reactions differing only in the ease with which electrons are transferred to the substrate. Ordinarily mercury metal does not react with alkyl halides because of its high ionization potential 240 kcal/mole as compared with 124,176 and 216 kcal/mole for lithium, magnesium and zinc respectively. However, if one places a potential across mercury then it will readily react with alkyl halides in an electrolytic reaction.

Controlled potential electrolysis[67] of (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane in acetonitrile at −2.7 volts vs. S.C.E. yielded the hydrocarbon (−)-(R)-1-methyl-2,2-diphenylcyclopropane with an optical purity of 25%. Current integration indicated that 1.98 electrons per molecule reacted. The reduction involves two single electron transfers (SET).



(+)-(S) (−)-(R)

The reduction is viewed as occurring in the following manner.[68]

(1) $\mathrm{RBr} + e^- \rightarrow [\mathrm{R{\div}Br}]^-$

(2) $[\mathrm{R{\div}Br}]^- \rightarrow \mathrm{R}\cdot + \mathrm{Br}^-$

(3) $\mathrm{R}^{\cdot} + e^- \rightarrow \mathrm{R}{:}^-$

(4) $\mathrm{R}^{\cdot} + \mathrm{Hg}^{\circ} \rightarrow \mathrm{R\text{-}Hg}_n^{\cdot}$

(5) $\mathrm{RHg}_n^{\cdot} + e^- \rightarrow \mathrm{R}{:}^- + \mathrm{Hg}_n^{\circ}$

(6) $\mathrm{R\text{-}Hg}_n^{\cdot} + \mathrm{R\text{-}Hg}_n^{\cdot} \rightarrow \mathrm{R\text{-}Hg}_n\text{-}\mathrm{R} \rightarrow \mathrm{RHgR} + \mathrm{Hg}_{n-1}^{\circ}$

(7) $\mathrm{R\text{-}Hg\text{-}R} + e^- \rightarrow \mathrm{R}{:}^- + \mathrm{RHg}^{\cdot} \xrightarrow{\mathrm{Hg}^{\circ}} \mathrm{RHg}_n^{\cdot}$

(8) $\mathrm{R}^- + \mathrm{CH_3CN} \rightarrow \mathrm{R\text{-}H} + {}^-\mathrm{CH_2CN}$

(9) $\mathrm{R}^- + (\mathrm{Et})_4\mathrm{N}^+\mathrm{Br}^- \rightarrow \mathrm{R\text{-}H} + \mathrm{CH_2} = \mathrm{CH_2} + (\mathrm{Et})_3\mathrm{N} + \mathrm{Br}^-$

As in direct metallation, the reaction occurs at the metal surface. An electron is transferred from the surface to the σ^* antibonding orbital of the carbon-bromine bond to produce the anion-radical in the rate determining step[67] (1). The anion-radical can then dissociate at the surface to the 1-methyl-2,2-diphenylcyclopropyl radical (2). At this point some racemization may occur and the radical can undergo a number of indistinguishable reactions. The radical may pick up another electron to yield the anion (3) or since mercury is such an efficient radical trap, the radical may become adsorbed on the mercury surface (4) from which it can either take another electron to yield the anion (5) or combine with another adsorbed radical to produce a dicyclopropylmercury (6).

The formation of the dicyclopropylmercury alone or in combination with the adsorbed radical type intermediates accounts for the observation that the substrate disappears at a faster rate than the product appears.[67,68] The dicyclopropylmercury radical can then accept an electron to produce the anion and a cyclopropylmercury radical which in combination with the mercury surface becomes an adsorbed radical (7) which can be recycled through pathway (5) or (6). The anions formed in (3), (5), and (7) react at the surface with acetonitrile solvent (8) to yield the hydrocarbon. When $\mathrm{CD_3CN}$ was used the hydrocarbon isolated contained 76% deuterium[68]. The anion can also react with the electrolyte, tetraethylammonium bromide, in an elimination reaction (9) to produce hydrocarbon, ethylene and triethylamine, all of which have been identified in the reaction mixture.[67]

The reaction of lithium metal with the same chiral (+)-(S) bromide produces a product which has retained its optical activity to the extent of 46%.[53] Reaction with magnesium results in 18% retention of optical activity with overall retention of configuration.[60] The observation that the hydrocarbon produced in electrolytic reduction has retained 25% of its optical activity (63% retention of configuration) is consistent with the proposed surface nature of this reaction.

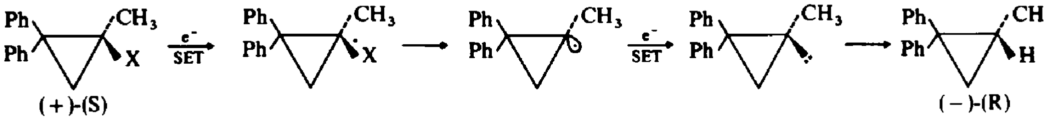
The controlled potential electrolysis of *endo*-7-bromo-*exo*-7-chlorobicyclo[4.1.0]heptane and *exo*-7-bromo-*endo*-7-chloro-bicyclo-[4.1.0]heptane resulted in a mixture of *exo* and *endo*-7-chlorobicyclo[4.1.0] in which the retention-inversion ratio was 2.6:1 in each case. Overall retention of configuration is the usual observation.[67] However, this need not always be the case, since by changing the substituent at the reductive center from methyl, in 1-bromo-1-methyl-2,2-diphenylcyclopropane to a carboxyl or carbomethoxyl group, the resulting product was still optically active (30–40%) but the configuration was inverted.[65]

DISSOLVING METAL REDUCTIONS

The reduction of alkyl halides by solutions of dissolved metals provides a convenient means of removing halogens to produce hydrocarbons. It is generally accepted that these reductions involve free radical intermediates.[69] The mechanism involves two single electron transfers (SET).

$$R\text{-}X \xrightarrow{e^-} [R\dot{-}X]^- \rightarrow R^\cdot + X^- \xrightarrow{e^-} R\!:\! \xrightarrow{S-H} R\text{-}H$$

It is well established that the 1-methyl-2,2-diphenylcyclopropyl anion is capable of retaining its optical activity and configuration.[58,60] It has also been shown that when the corresponding radical is generated in solution the resulting product is racemic.[42,43] Because of these observations a study of the reduction of chiral 1-halo-1-methyl-2,2-diphenylcyclopropane with solutions of sodium in liquid ammonia was undertaken.[70] The stereochemical results observed were shown to be dependent on the concentration of sodium in ammonia, the halogen used and a heterogeneity factor.



X = Cl, Br, I

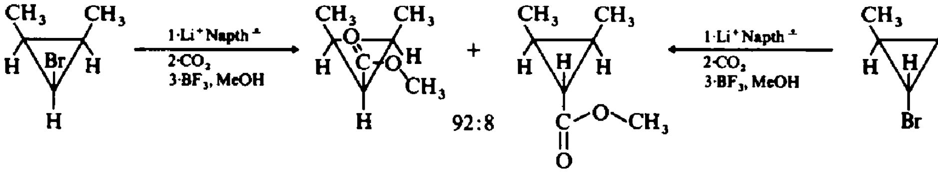
The chemical composition and physical properties of solutions of sodium in liquid ammonia have been known to depend upon the concentration. In particular, physical measurements have generally shown that such solutions pass from blue solutions where they contain essentially free solvated electrons at very high dilution (0.003 M), through solutions having saltlike characteristics (0.003–1.0M), to bronze solutions that behave as metals at very high concentration.[71] The reduction of (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane using a dilute solution (0.026M) of sodium in liquid ammonia yielded, *inter alia*, essentially *racemic* hydrocarbon. On the other hand, when a concentrated solution (6.5M) was used the hydrocarbon produced was 46% optically pure with overall retention of configuration. These results are consistent with the interpretation that under dilute conditions the cyclopropyl radical is produced in solution and before the second SET occurs it racemizes. At high concentrations, (metallic bronze) the reaction is occurring at the metallic surface leading to a stereochemical result comparable to that observed with metallic sodium in ether.[60]

Moreover, the effect of halogen on the stereochemical course of the reduction is in the same order as that observed on metallic surfaces. The optical purity of the hydrocarbon, using 4M solution of sodium in liquid ammonia, decreases in going from chloride (58%) to bromide (43%) to iodide (17%).

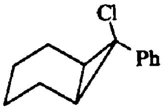
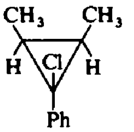
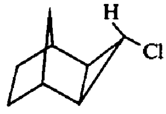
The above interpretation would seem adequate to account for the results. However, the reaction is of greater complexity and may not involve a metal surface at all. If instead of adding *crystalline* chiral (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane to a 3–4M solution of sodium in ammonia to obtain the hydrocarbon of 43% optical purity, one adds an ammoniacal *solution* of the bromide to the dissolving metal solution then the resultant hydrocarbon is completely racemic. It is tempting to speculate that the observed optical activity in the product, when crystals are used, is due to the radical being formed and trapped at the surface of the crystal lattice. It is noteworthy that the crystals turn a deep red as soon as they are added to the dissolving metal solution. Since most organic halides have limited solubility in liquid ammonia these results point out a danger in the interpretation of results obtained in such media. However, it is clear that when the 1-methyl-2,2-diphenylcyclopropyl σ radical is produced *in solution* under dilute dissolving metal conditions (Na/NH_3) it is incapable of maintaining its configuration and that its inversion frequency is greater than a second SET.

The effect of concentration on the stereochemical consequences of sodium naphthalenide (0.4M in dimethoxyethane) reduction of chiral 1-isocyano-1-methyl-2,2-diphenylcyclopropane is similar to that observed for the corresponding 1-bromo derivative.[72] At low concentrations the hydrocarbon produced is essentially racemic whereas at higher concentrations the optical purity is as high as 13% with overall retention of configuration. Jacobus[73] has reported that reduction of chiral 1-bromo-1-methyl-2,2-diphenylcyclopropane with sodium naphthalenide in dimethoxyethane (0.5M) yields the corresponding hydrocarbon of 29% optical purity with net retention of configuration. This observation was interpreted to mean that the 1-methyl-2,2-diphenylcyclopropyl σ radical was being captured by a second SET at a rate faster than its inversion frequency.

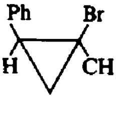
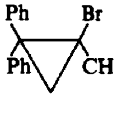
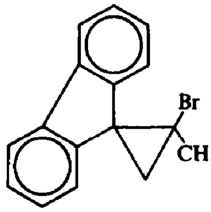
This conclusion was challenged by Boche[74] who showed that the following pairs of geometric isomers each gave an identical product mixture when reduced with solutions of lithium naphthalenide followed by carboxylation and methylation. This observation indicates that the second SET was not faster than the inversion frequency of the σ radical intermediate. This view is supported by others[50,75] who studied naphthalenide reductions of the following systems.



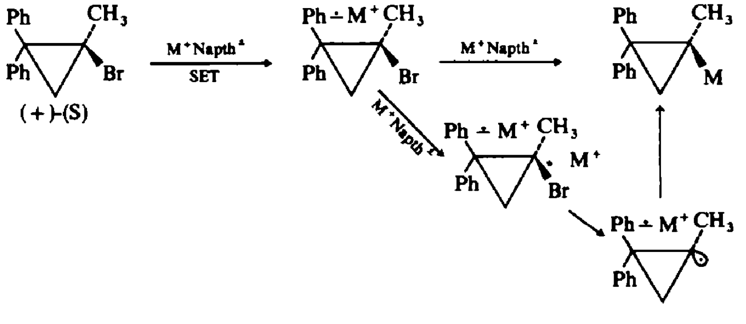
Recently[76] Boche has shown that the same result is obtained in the reduction of *cis*- and *trans*-1-bromo-1-methyl-2-phenylcyclopropane by alkali metal naphthalenides. Identical mixtures of the corresponding hydrocarbon are obtained from both *cis*- and *trans*-isomers. However, when a second phenyl substituent is placed in the 2-position or when a 2,2-biphenylene derivative is used the results

are quite different. Potassium naphthalenide reduction of chiral 1-bromo-1-methyl-2,2-diphenylcyclopropane and chiral 1-bromo-1-methyl-2,2-biphenylenecyclopropane yielded the corresponding hydrocarbon in 53% and 75% optical purity, thus confirming Jacobus results if not the interpretation.

To account for the retention of activity and configuration Boche has made the following interesting suggestion.[76] The biphenyl or biphenylene are good electron accepting substituents[77,78] and the first SET goes into the aromatic ring rather than the carbon-halogen bond, to produce a new ion radical intermediate. This intermediate can react with another M⁺Naphth⁻ in a second SET to produce the metallocyclopropane directly or the second SET can go into carbon-halogen σ^* antibonding orbital to produce a diradical dianion. The latter can either lose bromide ion to yield a diradical monoanion which collapses to the metallocyclopropane or it can collapse directly to the



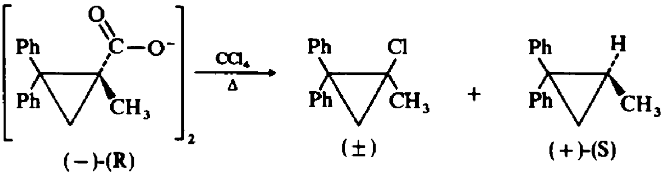
metallocyclopropane. Whichever pathway the reaction takes the important feature is that it involves intramolecular trapping of the radical. It is the equivalent of a solvent cage reaction which has been shown to lead to high retention of optical activity for the 1-methyl-2,2-diphenylcyclopropyl radical.[43] Comparable reactions have been interpreted recently in a similar manner.[78]

In summary, the interpretation of results obtained from dissolving metal reductions with regard to the cyclopropyl radical is fraught with pitfalls. The results obtained are dependent on concentration of the dissolved metal, nature of halogen, heterogeneity and types of substituents.

SOLVENT CAGE REACTIONS

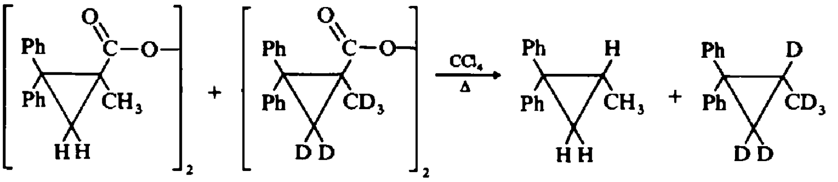
With the possible exception of certain dissolving metal reactions (*vide supra*), the 1-methyl-2,2-diphenylcyclopropyl σ radical, is incapable of maintaining its configuration in solution. In order to trap this cyclopropyl radical before complete recemization occurs, it must react at a rate equal to or greater than the inversion frequency estimated to be $\sim 10^8\,s^{-1}$. Since the average time required for diffusion from a cage has been estimated[79] to be $10^{11}s^{-1}$, the most likely place to intercept a rapidly inverting σ radical would be within a solvent cage.

The thermal decomposition of (−)-(R)-1-methyl-2,2-diphenylcyclopropanoyl peroxide in pure carbon tetrachloride yielded besides the expected (±)-1-chloro-1-methyl-2,2-diphenylcyclopropane

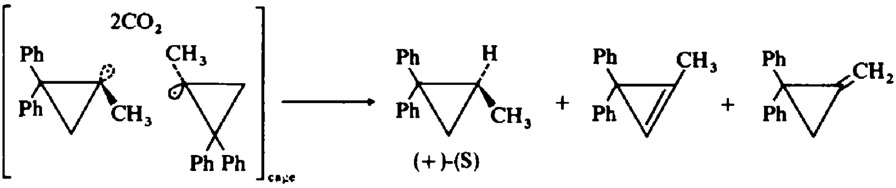


a 2% yield of (±)-(S)-1-methyl-2,2-diphenylcyclopropane.[43] Doubling the concentration of the peroxide had no effect on the yield of the hydrocarbon. Neither did addition of a good radical trap such as iodine. These observations are consistent with a solvent-cage disproportionation reaction.

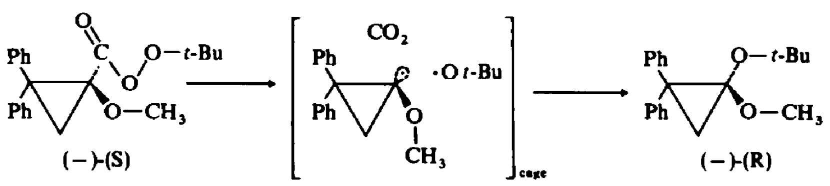
Finally the most definitive evidence for a cage reaction was the observation that when an equimolar mixture of the peroxide and the peroxide-d_{10} were decomposed no crossover products were obtained; only equal amounts of fully protonated hydrocarbon and the hydrocarbon-d_6.[43] The



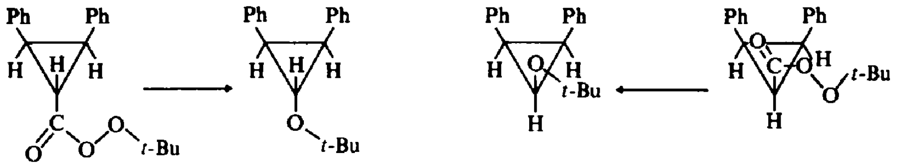
optical purity of the isolated (+)-(S)-1-methyl-2,2-diphenylcyclopropane was found to be 31–37% with a net retention of configuration. Thus, when the lifetime of the rapidly inverting σ radical is sufficiently great to permit diffusion out of the solvent cage the product formed by the radical reacting with the substrate (CCl_4) will be essentially racemic. If the radical is constrained in a solvent cage and reacts within that cage, it will maintain its configuration to a large extent.



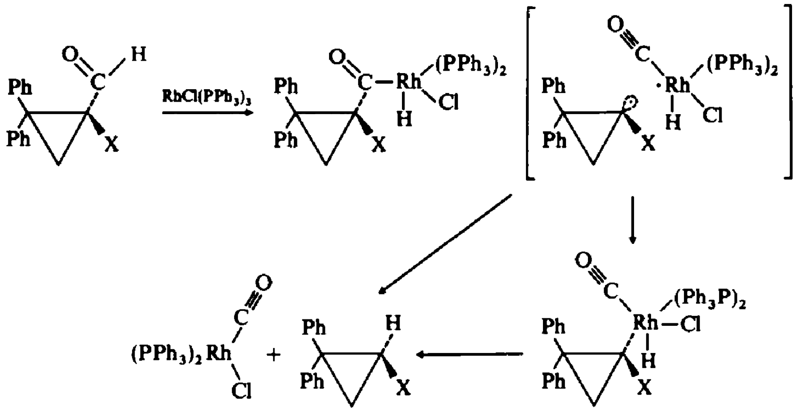
The disproportionation reaction is depicted above although other modes are possible.[43] β-Hydrogens are abstracted by the radical, either from the methyl group or the ring, to yield the hydrocarbon with largely retained configuration and the two olefins. A cage disproportionation reaction has also been observed in the thermal decomposition of *trans*-2-phenylcyclopropanoyl peroxide in carbon tetrachloride.



A cage recombination reaction takes place in the thermal decomposition of t-butyl (−)-(S)-1-methoxy-2,2-diphenylcyclopropane percarboxylate.[35] A 0.8% yield of 1-methoxyl-1-t-butoxy-2,2-diphenylcyclopropane, $[\alpha]^{24}_{\mathrm{Hg}}$-63°, was isolated from the reaction mixture. Unfortunately, neither the absolute configuration nor the optical purity of cage product was determined. The magnitude of the rotation would indicate that a high degree of retention of optical activity had occurred. In line with previous cage reactions the configuration is probably maintained as well.



Thermal decomposition of t-butyl *trans,trans*-2,3-diphenylcyclopropanepercarboxylate in ethylbenzene yielded (10%) exclusively *trans,trans*-2,3-diphenylcyclopropyl t-butyl ether as a cage recombination product, whereas the *cis,cis*-isomer gave a low yield of recombination product consisting of 1% *trans,trans* and 1.5% *cis,cis*.[80] The low yield and the loss of stereoselectivity in the latter case are thought to be due to a steric effect.[80]



It has been proposed that the decarbonylation of aldehydes by the Wilkinson catalyst $[RhCl(PPh_3)_3]$ involves a radical pair disproportionation or recombination reaction.[81] A radical pair intermediate in solution is equivalent to a cage reaction. Table 11 shows the results obtained from the decarbonylation of a series of chiral cyclopropyl aldehydes.[81,82]

Table 11. Decarbonylation of chiral 1-substituted-2,2-diphenylcyclopropanecarboxaldehydes[81]

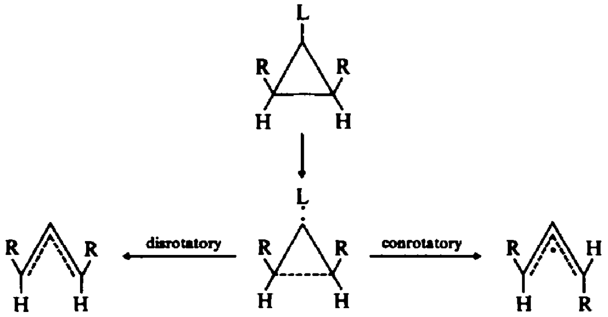
Substituent (−X)	Config.	Product, Config.	%Opt. Purity
CH_3	(+)-(R)	(+)-(S)	94
Cl	(+)-(S)	(+)-(S)	83
F	(−)-(S)	(−)-(S)	73
OCH_3	(−)-(S)	(+)-(S)	6

REARRANGEMENTS

The electrocyclic cyclopropyl radical-allyl radical rearrangement has been the subject of many theoretical investigations not all of which are in agreement.

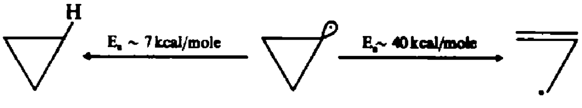
Woodward and Hoffmann[83] on the basis of extended Hückel calculations suggested that the conrotatory mode is slightly preferred. At the same time Longuet-Higgins[84] pointed out that both ring-opening modes were unfavorable because they are symmetry forbidden. *Ab initio* calculations by Farnell and Richards[85] supported this latter view. Other calculations[86] led to energies of activation in the range of 30–40 kcal/mole for disrotatory opening and 40–50 kcal/mole for conrotatory opening of the cyclopropylradical.

Haselbach's[87] analysis is of interest. His calculations indicated that the rupture of the ring *precedes* rotation of the resultant CH_2 groups. He is also in agreement with Longuet-Higgens[84] that

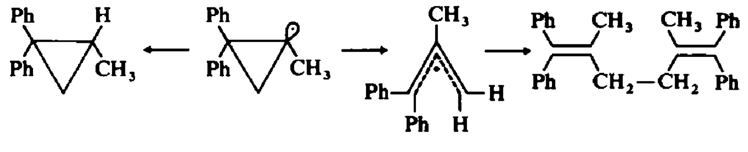


both electrocyclic modes of ring opening are unfavorable. He favors a disrotatory opening if "abstraction of the leaving group and ring opening occur in a concerted manner". This qualification would exclude a concerted electrocyclic reaction since it is known from esr observation and chemical evidence that the cyclopropyl radical exists in solution. To emphasize this point, it should be noted that in solution the unsubstituted cyclopropyl radical itself has never been observed to rearrange to the more stable allyl radical in spite of the 30 kcal/mole stabilization predicted for this rearrangement.

As we have previously discussed the cyclopropyl radical is a very reactive radical. When in addition we consider the high activation energy (~40 kcal/mole) necessary for the cyclopropyl radical to rearrange to the allyl radical we are not surprised that rearrangement is not always observed. The cyclopropyl radical prefers to react with solvent by abstracting hydrogen, the activation energy for which is reported[88] to be only ~7 kcal/mole.

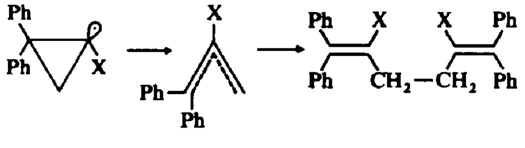


Only unrearranged cyclopropyl products were reported for photochemical chlorination[18,89] and vapor phase nitration[19] of cyclopropane. The Hunsdiecker reaction of silver cyclopropanecarboxylate[90] and the thermal decomposition of cyclopropanoyl peroxide[14] also gave exclusively unrearranged product as did the di-t-butyl peroxide initiated decarbonylation of 1-methyl



and 1-phenylcyclopropanecarboxaldehyde.[17] In general one can predict that when a good radical scavenger, solvent or substrate, is present in the reaction, unrearranged product will result (i.e. see Tables 8 and 9).

The first example of the rearrangement of a cyclopropyl radical to an allyl radical *in solution* was observed in the thermal decomposition of 1-methyl-2,2-diphenylcyclopropanecarbonyl peroxide.[42,43] The radical reacted by abstracting hydrogen from solvent or by rearranging to the 1,1-diphenyl-2-methylpropenyl radical which dimerized to yield 1,1,6,6-tetraphenyl-2,5-dimethyl-1,5-hexadiene. The proportion of dimeric product to that of cyclopropane is dependent on the solvent. If a good radical scavenger solvent is used, such as chloroform, carbon tetrachloride or thiophenol then only the unrearranged cyclopropane derivative is obtained. This is also the case when a radical trap such as iodine is added to a benzene solution.



X = H,CH_3,F,Cl,Br,OCH_3

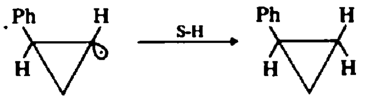
The ratio of dimeric product to cyclopropane product is a measure of the reactivity of the solvent toward the cyclopropyl radical. Table 12 shows the results of such a study.

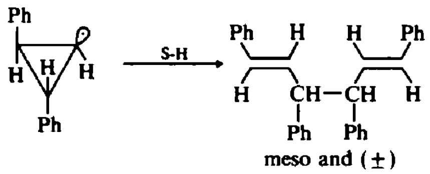
Table 12. Relative reactivity of various solvents toward the 1-methyl-2,2-diphenylcyclopropyl radical[43]

Solvent	Cyclopropane, %	Dimer, %	Relative React.[a] per active hydrogen
Benzene	5.85	11.95	0.23
Cyclohexane	3.98	7.14	0.30
t-Butanol	2.70	2.71	0.33
Acetone	6.77	6.77	0.51
Diethylether	7.37	9.61	0.57
Ethyl Acetate	4.25	7.50	0.92
Toluene	7.41	8.34	1.00
Methanol	1.49	1.27	1.24
Tetrahydrofuran	6.98	6.45	1.44
Acetonitrile	8.35	4.62	1.76
Ethylbenzene	4.32	3.82	1.77
Cumene	1.45	1.77	2.50
Ethanol	3.00	1.53	3.05
2-Propanol	4.08	2.71	4.40

(a)Expressed in terms of reactivity of toluene as 1.

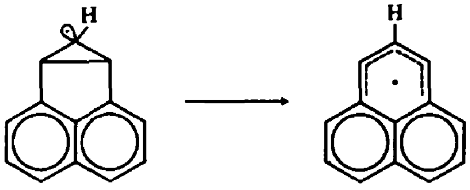
Similar rearrangements have been observed with 2,2-diphenylcyclopropyl radicals that have a variety of 1-substituents.[35]



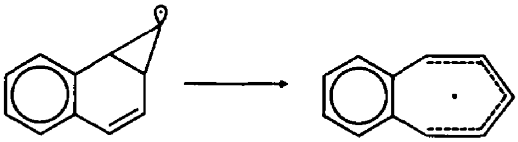


Chen[91] has demonstrated that one phenyl group in the 2-position of the cyclopropyl radical is insufficient to overcome the activation energy necessary to obtain the rearrangement. Thus thermal decomposition of *trans*-2-phenylcyclopropanecarbonyl peroxide in a poor hydrogen donating solvent such as benzene yielded only 2-phenylcyclopropane. However, when two phenyl groups were located in the 2,3-position of the cyclopropane ring rearranged product was obtained. Thus, under the same conditions, thermolysis of *cis,trans*-2,3-diphenylcyclopropanecarbonyl peroxide gave a 30% yield of 1,3,4,6-tetraphenyl-1,5-hexadiene. Rüchardt[80] has confirmed this result and has also shown that *cis,cis* and *trans,trans*-isomeric peroxide produced the same 1:1 mixture of rearranged products. An attempt to interpret these results on the basis of an electrocyclic ring opening did not result in any definitive conclusions.[80] The following cyclopropyl radicals have also been shown to undergo rearrangement. In each case the rearranged radical is a highly delocalized intermediate thereby reducing the activation energy sufficiently for the rearrangement process to occur.

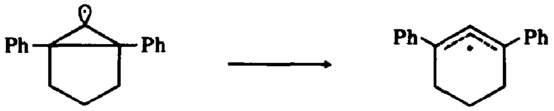
1[92]



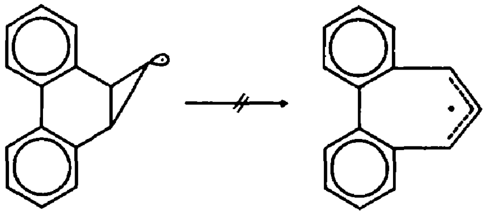
2[93]



3[92b]



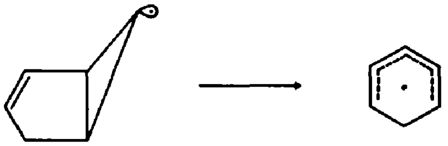
4[92b]



Surprisingly the dibenzonorcaradien-7-yl radical (reaction 4) is reported[92b] not to rearrange to the dibenzotropyl radical. The ring opening of 2-bicyclo [1.1.0]butyl radical[94] is not surprising, due to the strain and cyclopropyl carbinyl nature of the radical. Rearrangements of other bicyclic systems[95,96] such as *b-d* would not be expected.

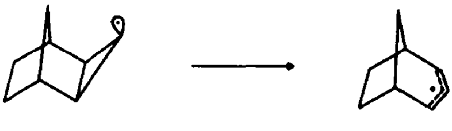
(a)

(b)



(c)

(d)



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