AN ABSTRACT OF THE THESIS OF

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Title: Part I. The Identity of the Chain Propagating Radical(s) in Photoinitiated Benzylic Bromination with Bromotrichloromethane. Part II. Chlorine Atom Abstraction from α- and β-Chloroepoxides by the Triphenyltin Radical.

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Abstract approved: _____

Gerald J. Gleicher

The relative rates of hydrogen atom abstraction from *meta*- and *para*-substituted toluenes under conditions of benzylic bromination by bromotrichloromethane were determined at 70°C. The magnitude of the Hammett rho value for these reactions was found to be dependent on the method of initiation. When the reaction is initiated with light, the rho value is -0.70. When thermal initiation is used, the rho value is -0.38. These differences are interpreted in terms of two competing mechanisms, for the photoinitiated reactions, involving hydrogen atom abstraction by the trichloromethyl radical in one case and by the bromine atom in the other. Thermal initiation involves hydrogen atom abstraction only by the trichloromethyl radical. The relative rates for benzylic bromination of unsubstituted alkylbenzenes with bromotrichloromethane support this interpretation and demonstrate a greater sensitivity to steric hindrance when thermal initiation is utilized. This is the result of sole participation of the bulkier trichloromethyl radical.

The relative rates of reaction for α- and β-chloroepoxides with triphenyltin

radicals at 70°C have also been determined. α-Chloroepoxides react at a much lower rate than do β-chloroepoxides. The nature of the increased reactivity of the β-chloroepoxides has been investigated by studying two pair of diastereomers and an acyclic β-chloroether. The results are discussed in terms of the inductive, resonance, and stereoelectronic effects of the epoxide.

The rate of ring opening rearrangement of β-epoxy radicals has been estimated by investigation of intramolecular competition with cyclopropylcarbinyl radical rearrangement. Generation of cyclopropyloxiranylmethyl radicals and trapping with triphenyltin hydride gave only products derived from ring opening of the epoxide ring. A kinetic analysis, using rate data from the literature, allowed determination of lower limits for the rate constant of β-epoxy radical rearrangement.

Part I. The Identity of the Chain Propagating Radical(s) in Photoinitiated Benzylic Bromination by Bromotrichloromethane.
Part II. Chlorine Atom Abstraction from α- and β-Chloroepoxides by the Triphenyltin Radical.

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Date thesis is presented November 13, 1991

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DEDICATION

To Pamela--Without you, I doubt that this thesis would ever have been written. It is dedicated to you. I love you.

To my parents--Your love of God, your love of each other, and your love for me are the three gifts I will always cherish.

To Herman and Pat--The support of family on all sides makes each of life's risks a little safer.

Not only so, but we also rejoice in our sufferings, because we know that suffering produces perseverance; perseverance, character; and character, hope. And hope does not disappoint us, because God has poured out his love into our hearts by the Holy Spirit, whom he has given us. (Romans 5:2-5).

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Introduction

"A mechanism is the actual process by means of which a reaction takes place--which bonds are broken, in what order, how many steps are involved, the relative rate of each step, etc. In order to state a mechanism completely, we should have to specify the positions of all atoms, including those in solvent molecules, and the energy of the system, at every point in the process. A proposed mechanism must fit all the facts available. It is always subject to change as new facts are discovered. The usual course of a discovery is that the gross features of a mechanism are the first to be known, and that increasing attention is paid to finer details. The tendency is always to probe more deeply, to get more detailed descriptions."[1]

The search for mechanistic understanding of free-radical reactions began in 1900. In that year, Moses Gomberg correctly proposed the intermediacy of triphenylmethyl,[2] a trivalent carbon species, in reactions that allegedly formed hexaphenylethane. Gomberg, who asked that the field of free-radical chemistry be left to his exclusive study, and several other chemists who ignored his request, spent the first decades of the century focusing on the grossest of mechanistic details: the identity of the intermediates and products. The resulting disagreements,[3] sometimes heated, were not settled until almost seventy years later.[4]

Another mile-stone in free radical chemistry occurred in 1937 when Kharasch and co-workers proposed a chain mechanism for the anti-Markovnikov addition of hydrogen bromide to terminal olefins.[5] Since then, a large number of free-radical

reactions have been shown to proceed *via* chain mechanisms that involve initiation, propagation, and termination steps. Free-radical addition reactions of this type have been extensively studied.[6]

Reactions that involve atom abstraction from a substrate by a free-radical form another important and widely studied class.[7] The vast majority of reactions of this type involve abstraction of either a hydrogen atom or a halogen atom. Many of these abstraction reactions have shown a marked dependence of rate on substrate structure, as shown by a number of Hammett linear free energy studies. Table 1 contains Hammett rho values for several hydrogen abstraction reactions from substituted toluenes.

Table 1. Rho values for hydrogen atom abstraction reactions from substituted toluenes by a variety of radicals.

Abstracting Agent	T(°C)	Rho[a]	reference
Br·	80	-1.4 (σ^+)	8
Cl·	40	-0.7 (σ^+)	9
t-BuO·	40	-0.4 (σ^+)	10
Undecyl·	80	+0.5 (σ)	11
t-Bu·	80	+0.7 (σ)	12

a) Substituent constants leading to optimal correlation shown.

The nature of the polar effect on the rates of atom abstraction reactions can be addressed by considering the possible resonance contributors to the transition state

(Figure 1).

$$[ArCH_2\text{--}H \;\; \overset{\cdot}{X}] \leftrightarrow [\overset{\cdot}{Ar}CH_2 \;\; H\text{----}X] \leftrightarrow [\overset{+}{Ar}CH_2 \;\; \overset{\cdot}{H} \;\; \overset{-}{:}X] \leftrightarrow [\overset{\cdot\cdot}{Ar}CH_2 \;\; \overset{\cdot}{H} \;\; \overset{+}{X}]$$

I II III IV

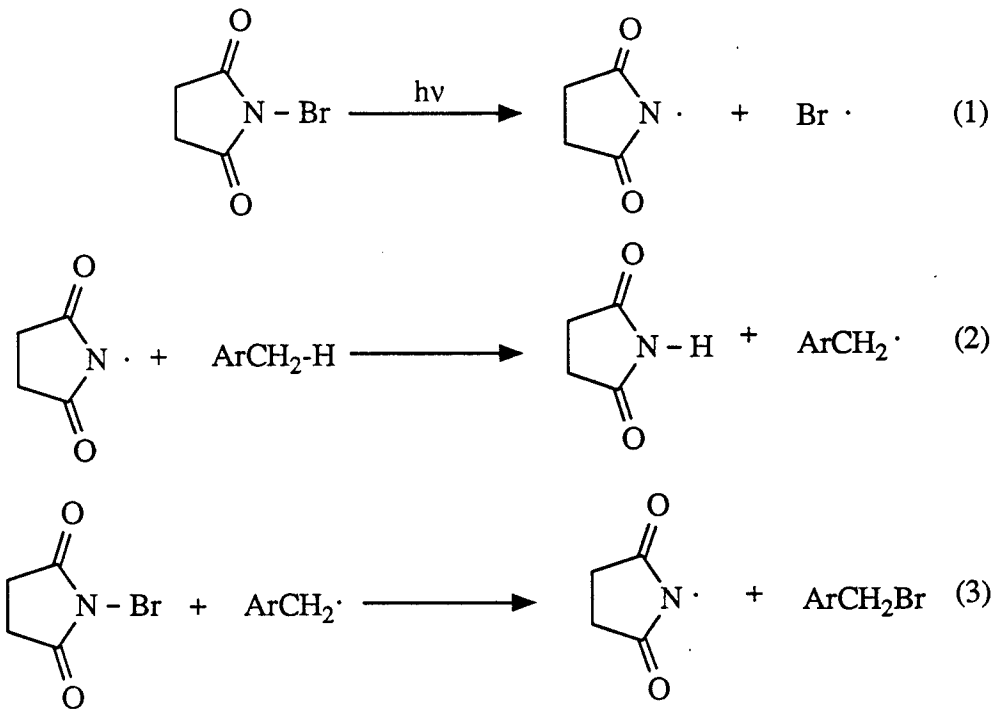
Figure 1. Canonical forms of the transition state of benzylic hydrogen atom abstraction.

For abstracting radicals that are more electronegative than the benzylic carbon, canonical form III should be an important contributor and substituents which can stabilize positive charge will accelerate the reaction. Examples of such radicals include bromine atom, chlorine atom, and *tert*-butoxyl, radical all of which yield negative rho values. Optimum correlation has been achieved with sigma-plus constants for each of these radicals, again demonstrating the importance of positive charge development in the transition state. Radicals of this type are termed electrophilic. Conversely, reactions in which the abstracting radical is less electronegative than the benzylic carbon will rely on a greater contribution from canonical form IV, and substituents which can stabilize negative charge will accelerate the reaction. Nucleophilic radicals include *tert*-butyl and undecyl, both of which demonstrate positive rho values when correlated with Hammett sigma constants. Substituents which would demonstrate differences in correlation for sigma and sigma-minus, i.e. pi-acceptors in the para position, unfortunately were not employed in either study.[11,12]

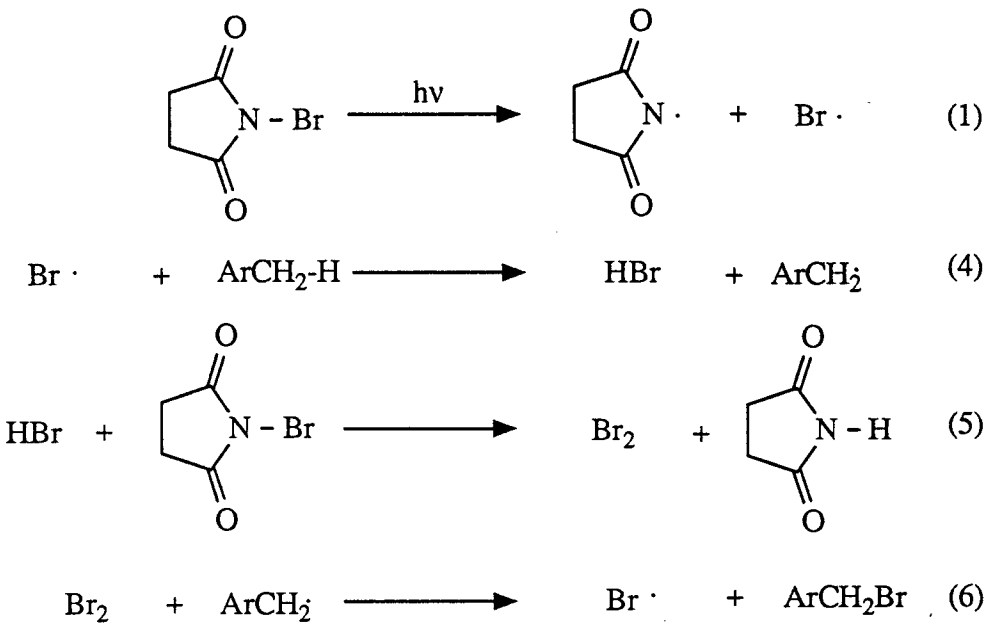
This model involving charge separation in the transition state of atom abstraction reactions has not been without its dissenters. Zavitsas and Pinto argued that all of the experimental evidence then available (circa 1972) could be explained based

on the dependence of the strength of the benzylic carbon-hydrogen bond toward substituent variation.[13] Electron donating groups accelerate hydrogen atom abstraction, according this theory, only by weakening the bond between the hydrogen and the benzylic carbon. This theory has been disregarded due to its failure to explain positive rho values for nucleophilic radicals like *tert*-butyl[12] and undecyl.[11]

The identity of the abstracting radical is not always obvious from experimental conditions and often two or more mechanisms may be written which can account for the observed products. Photoinitiated bromination of toluene using N-bromosuccinimide (NBS) is an example of a reaction where the identity of the hydrogen abstracting species was in question. Originally, a mechanism involving hydrogen atom abstraction by a succinimidyl radical was proposed by Bloomfield (Scheme 1).[14] Later, Goldfinger proposed an alternative mechanism which involved hydrogen atom abstraction by bromine atom (Scheme 2).[15]



Scheme 1. Succinimidyl radical mechanism for benzylic brominations by NBS.



Scheme 2. Bromine atom mechanism for benzylic brominations by NBS.

The bromine atom mechanism is now widely accepted as correct. This is predominately due to studies by Pearson and Martin.[16] They reported rho values for benzylic bromination using molecular bromine, NBS, tetramethyl-NBS, and tetrafluoro-NBS. In certain cases two temperatures were employed. The similarity of the rho values (Table 2) is convincing evidence that the hydrogen abstracting agent is the same in each case; namely bromine atom.

Table 2. Rho values for benzylic brominations of subtituted toluenes with a variety of brominating agents.[a]

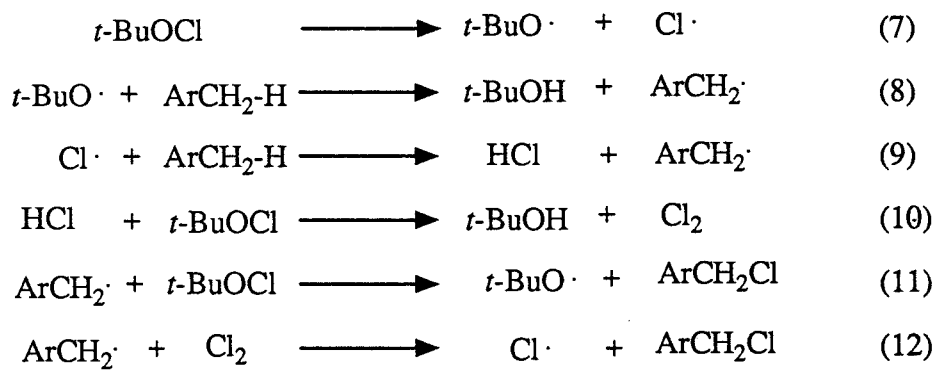
Brominating Agent	rho (19°C)	rho (80°C)
molecular bromine	-1.76	-1.36
N-bromosuccinimide		-1.46
N-bromotetramethylsuccinimide	-1.79	-1.36
N-bromotetrafluorosuccinimide		-1.45

a)Reference 16.

Pearson and Martin also showed that earlier differences in the rho values for bromine and NBS, a major hindrance to acceptance of the Goldfinger mechanism, were due to participation of hydrogen bromide when bromine was in excess.

tert-Butyl hypochlorite is another reagent for which the identity of the hydrogen abstracting species has been investigated. This reagent has been shown to be very effective as a chlorinating agent. Walling and co-workers have reported on its utility, reactivity, and mechanism.[17] Scheme 3 shows an elaborate mechanism for

chlorinations using *t*-butyl hypochlorite that includes hydrogen abstraction by both *tert*-butoxyl radical and chlorine atom. Walling and McGuinness have shown that different selectivities are observed for *t*-butyl hypochlorite chlorinations in the presence and absence of a chlorine atom trap.[17] They found that the addition of small amounts of trichloroethylene was effective in stopping chlorine atom chain propagation. They have estimated that under normal conditions, about half the hydrogen atom abstractions are due to chlorine atom (eq. 9) while the other half are due to *tert*-butoxyl (eq. 8).



Scheme 3. Benzylic chlorination with *t*-butyl hypochlorite.

Although they have not been studied to the same extent as hydrogen atom abstractions, halogen atom abstractions have more recently received a great deal of attention. Halogen atom abstractions by silicon, germanium, and tin centered radicals have been investigated. Kuivila has reviewed the reactions of trialkyltin hydrides with organic halides.[18] He has shown that for chlorine atom abstractions by trialkyltin radicals the rate determining step is chlorine atom transfer. For abstraction of a halogen atom from a benzylic position by a trialkyltin or triaryltin radical, the order of reactivity is F << Cl < Br < I. For each series, the reactivity order is primary < secondary < tertiary. These reactions show a sensitivity to substituents which is

analogous to that observed for hydrogen atom abstractions. A similar model involving charge separated resonance forms for the transition state has been used (Figure 2).[18]

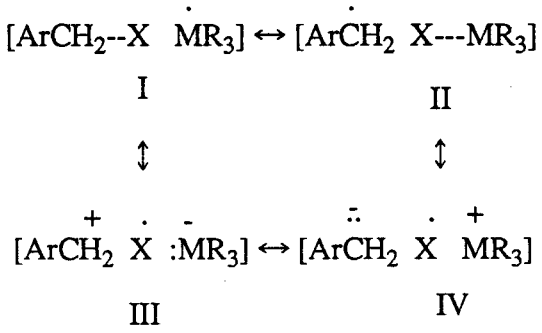


Figure 2. Canonical forms of the transition state of benzylic halogen atom abstraction by triorganotin radicals.

The electropositive nature of the metal suggests that canonical form IV should be an important contributor to the structure of the transition state. The development of negative charge at the halogen bearing carbon is evidenced by the observation of positive rho values for each of the halogens when reacted with triorganotin hydride (Table 3).[19] In each case, optimum correlation was obtained with sigma minus constants, suggesting that resonance stabilization of negative charge at the benzylic carbon is important in the transition state.

Table 3. Rho values for reactions of benzyl halides with tributyltin hydride at 90°.[a]

Halogen	rho[b]	Correlation coefficient
Chlorine	0.34	0.97
Bromine	0.17	0.98
Iodine	0.81	0.99

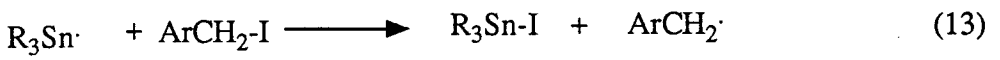
a) Reference 19.

b) Optimum correlations. All utilize sigma-minus substituent constants.

The nature of the transition state for these reactions has been investigated by several groups.[19-21] Blackburn and Tanner showed that substituted benzyl iodides demonstrate a much larger sensitivity to substitution than is observed for the corresponding chlorides or bromides.[19] While the chlorine and bromine cases follow the generally expected trend that more reactive substrates should show less sensitivity to substituent variation, iodine deviates greatly from this trend. The greater reactivity of benzyl iodides[18] coupled with the greater sensitivity to substituent variation indicate that a different mechanism must be operative. Blackburn and Tanner have proposed two possible alternative mechanisms for reaction of the benzyl iodides. The first involves the formation of a hypervalent iodine species (eqs. 14 and 15). An analogous mechanism was proposed by Sakurai for the reactions of triethylgermanium radical.[22] The second involves a single electron transfer in the rate determining step, to generate a radical anion (eqs. 16 and 17). Kochi *et al.* and Gleicher *et al.* have published reports

Halogen Atom Transfer Step (proposed alternatives).

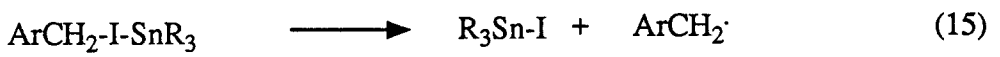
a) Dirrect Atom Abstraction.



(13)

b) Divalent Iodine Intermediate.

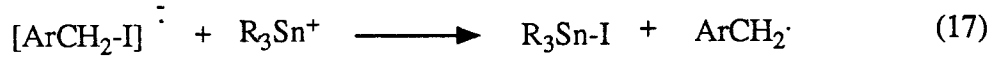
(14)



(15)

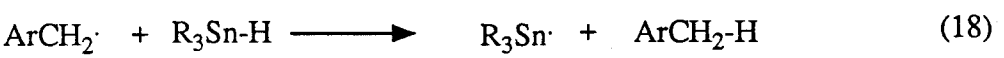
c) Single Electron Transfer.

(16)



(17)

Hydrogen Atom Transfer Step (common to all mechanisms).



(18)

Scheme 4. Proposed mechanisms for reaction of benzyl iodides.

which support an electron transfer mechanism for reaction of benzyl iodides. Kochi reported the carbon isotope effects for reaction of methyl iodide, methyl bromide, and methyl chloride.[20] He found evidence for extensive bond breaking in the transition states of the chloride and bromide cases. This is consistent with the relatively late transition state which might be expected for direct atom abstraction. In contrast, the isotope effect for methyl iodide was relatively small, suggesting a different mechanism was operative. Gleicher and co-workers found that the relative reactivities of several polycyclic iodomethylarenes with triphenyltin hydride correlated best with calculated energies of the corresponding radical anions.[21] They also suggested an electron transfer mechanism and proposed that the electron was transferred to an anti-bonding sigma orbital of the carbon-iodine bond.

The above results are consistent with a mechanistic dualism that involves direct

atom abstraction as the rate determining step for reactions of benzyl and alkyl chlorides and bromides, and single electron transfer for reactions of benzyl and alkyl iodides.

Part I. The Identity of the Chain Propagating Radical(s) in Photoinitiated Benzylic Bromination with Bromotrichloromethane.

Discussion of the Problem

The photoinitiated free-radical reactions of bromotrichloromethane date back to 1947 when Kharasch and co-workers reported its addition to a series of olefins.[23] In this account, they proposed a chain mechanism that is still accepted today (Scheme 5). Key in this mechanism is the rate-determining addition of the trichloromethyl radical to the less substituted end of the double bond in order to generate the more stable intermediate radical (eq. 20).

$$BrCCl_3 \xrightarrow{h\nu} Cl_3C\cdot + Br\cdot \quad (19)$$

$$RCH{=}CH_2 + Cl_3C\cdot \longrightarrow R\dot{C}H\text{-}CH_2\text{-}CCl_3 \quad (20)$$

$$R\dot{C}H\text{-}CH_2\text{-}CCl_3 + BrCCl_3 \longrightarrow RCHBr\text{-}CH_2\text{-}CCl_3 + Cl_3C\cdot \quad (21)$$

Scheme 5. Mechanism for radical addition of $BrCCl_3$ to olefins.

Kharasch also reported the observation of allylic hydrogen atom abstraction (as evidenced by the formation of chloroform) in competition with addition for the reaction of some olefins with bromotrichloromethane.[24] Huyser later showed allylic hydrogen atom abstraction, which is the rate determining step for bromination, could be comparable to addition if the lability of the hydrogen atom is increased or the accessibility of the double bond is decreased (Table 4).[25]

Table 4. Relative rates of addition versus allylic bromination for $BrCCl_3$ with several olefins at 78°.[a]

Olefin	$k_{add}/k_{brom.}$	Olefin	$k_{add}/k_{brom.}$
1-Octene	43	Cycloheptene	5.5
1-Decene	43	Cyclopentene	5.4
2-Pentene	5.7	Cyclohexene	1.2
3-Heptene	3.5	4-Methyl-2-pentene	1.3

a)Reference 25.

Citing unpublished work, Heiba and Anderson[26] closed a paper on γ-ray initiated additions of bromotrichloromethane with the observation that; "Bromotrichloromethane has been found to brominate selectively the α-carbon of an aromatic side chain." This statement was not expanded upon until three years later, in 1960 when Huyser published two papers which detailed his extensive study of benzylic bromination with bromotrichloromethane.[27,28]

In the first of these papers, Huyser demonstrated that photoinitiated reaction with bromotrichloromethane was a general method for bromination at the benzylic position of a number of alkylbenzenes.[27] He proposed a mechanism for benzylic bromination which involved hydrogen atom abstraction by the trichloromethyl radical as the rate determining step (Scheme 6). In the second paper, He reported the relative

$$BrCCl_3 \xrightarrow{h\nu} Cl_3C\cdot + Br\cdot \quad (19)$$

$$ArCH_2\text{-}H + Cl_3C\cdot \longrightarrow ArCH_2\cdot + HCCl_3 \quad (22)$$

$$ArCH_2\cdot + BrCCl_3 \longrightarrow ArCH_2Br + Cl_3C\cdot \quad (23)$$

Scheme 6. Mechanism for benzylic bromination by $BrCCl_3$.

rates of reaction of a series of substituted toluenes with bromotrichloromethane at 50°C.[28] A rho value of -1.46 was obtained when sigma plus constants were used. Huyser suggested that the observed polar effect may be due to contribution, to the transition state for hydrogen atom abstraction, of a charge separated resonance form like the one shown in equation 24.

$$ArCH_2\text{-}H + Cl_3C\cdot \longrightarrow [Ar\overset{+}{C}H_2 \quad \overset{\cdot}{H} \quad :\overset{-}{C}Cl_3] \longrightarrow ArCH_2\cdot + HCCl_3 \quad (24)$$

A second possible mechanism of photoinitiated benzylic bromination by bromotrichloromethane has been postulated on several occasions (Scheme 7).[29-32]

$$BrCCl_3 \xrightarrow{h\nu} Cl_3C\cdot + Br\cdot \quad (19)$$

$$ArCH_2\text{-}H + Br\cdot \rightleftharpoons ArCH_2\cdot + HBr \quad (25)$$

$$HBr + Cl_3C\cdot \longrightarrow Br\cdot + HCCl_3 \quad (26)$$

$$ArCH_2\cdot + BrCCl_3 \longrightarrow ArCH_2Br + Cl_3C\cdot \quad (23)$$

Scheme 7. Alternative mechanism for benzylic bromination by $BrCCl_3$.

McGrath and Tedder were the first to acknowledge this alternative mechanism as a possibility in gas-phase brominations with bromotrichloromethane.[29] They discounted

it on the basis that only brominated products and chloroform were observed. Likewise, Russell and DeBoer recognized the possibility of a bromine atom propagation mechanism but held that it could not explain observed differences in selectivity for reactions with molecular bromine.[30] Support for this mechanism was reported by Tanner and co-workers.[31,32] They suggested that this mechanism was in fact operative in photoinitiated brominations with bromotrichloromethane. This suggestion was based on results for a reinvestigation of structure reactivity behavior of bromotrichloromethane with substituted toluenes and unsubstituted alkylbenzenes, with and without a hydrogen bromide trap present. The supporting evidence for this alternate mechanism can be summarized as follows:

1) Differing rho values for the bromination of substituted toluenes were observed when the reactions were run in the presence of 20% added ethylene oxide or 10% added potassium carbonate. Either of these additives can function as a hydrogen bromide trap, apparently effective at shutting down equation 25 and forcing a change in mechanism to involve the trichloromethyl radical. When no additive was present, a rho value of -1.24 was observed, and compared with a rho value of -0.69 for reactions with 20% ethylene oxide added. Both correlations utilized sigma-plus substituent constants.

2) When mixtures of toluene and toluene-α-d_3 were reacted with bromotrichloromethane, analysis of the unreacted toluenes by mass spectroscopy showed that a large amount of deuterium scrambling had occurred. However, when the same reaction was run with added ethylene oxide or potassium carbonate, the scrambling of deuterium was greatly reduced or eliminated (Table 5). It was

Table 5. Deuterium scrambling between toluene and toluene-α-d_3 in reaction with $BrCCl_3$.[a]

Additive	% conversion of $BrCCl_3$	d_0	d_1	d_2	d_3
	0	48.5	0.0	0.9	50.6
none	59	15.3	32.8	33.9	18.0
none	58	13.6	31.4	35.2	19.8
none	49	14.3	29.2	33.6	22.9
ethylene oxide (20%)	7	47.8	0.0	0.9	51.3
ethylene oxide (20%)	96	42.5	0.0	2.0	55.5
potassium carbonate (10%)	58	37.6	3.2	3.5	55.7

a)Reference 31.

estimated that for toluene, the number of exchanges was more than three times the number of reactions with bromotrichloromethane. The reversibility of equation 25 is key to Tanner's explanation of the deuterium scrambling results. The reversibility of this step has been shown to decrease the sensitivity to substituent variation, making the rho value less negative when the brominations are carried out using molecular bromine instead of bromotrichloromethane.[16]

3) A reinvestigation of work by Russell and DeBoer[30] on the relative reactivity of toluene, ethylbenzene, and cumene was carried out. Here again the addition of hydrogen bromide scavengers has a dramatic effect on the observed reactivities (Table 6). The trichloromethyl radical is apparently much less sensitive to the

Table 6. Relative reactivity of primary, secondary, and tertiary benzylic hydrogen atoms with $BrCCl_3$.

Additive	Toluene : Ethylbenzene : Cumene	Reference
none	1.0:50:288	30
none	1.0:50:260	32
potassium carbonate	1.0:10.2:29.9	32
ethylene oxide	1.0:10.4:28.1	32

substrate structure.

These results demonstrate the complexity of photoinitiated brominations with bromotrichloromethane. Furthermore, it is apparent that the original mechanism, proposed by Huyser, is not sufficient to explain the observed reactivity changes in the presence of hydrogen bromide traps. However, several issues must be examined before accepting a mechanism involving chain propagation solely by bromine atom:

1) A large number of structure reactivity studies have been done which allow direct comparison of bromination methods. The results consistently show different selectivities for bromination with bromotrichloromethane when compared with other methods of bromination that are known to involve hydrogen atom abstraction by the bromine atom, i.e. molecular bromine or NBS (Table 7).

Table 7. Direct comparison of rho values for bromination with NBS and $BrCCl_3$ of several series of substituted alkylbenzenes.

Substrate	Temp. (°C)	Rho values[a] NBS	$BrCCl_3$	Ref.
Ethylbenzenes	80	-0.86	-0.53	33,34
Neopentylbenzenes	70	-0.75	-0.94	35
Cumenes	70	-0.29	-0.67	36
Allylbenzenes	70	-0.76	-0.39	37
Benzyl methyl ethers	80	-0.35	-0.36	38
α,α-Dimethoxytoluenes	80	-0.38	-0.18	38

a) All correlations utilize sigma-plus substituent constants.

2) Hydrogen atom abstraction from toluene by the trichloromethyl radical is predicted to be exothermic by 10.7 kcal/mole. Hydrogen atom abstraction from toluene by bromine atom is less exothermic, with a predicted gain in enthalpy of 2.8 kcal/mole.[31] While thermodynamic factors do not dictate reaction rates, it is important to note that chain propagation by either radical is energetically favorable, with trichloromethyl being more so.

3) The proposed bromine atom propagation mechanism requires reaction between two species which are both present at steady state concentrations. This requirement is forced at two different points in the mechanism. The first, when the incipient

benzyl radical reacts with steady state concentrations hydrogen bromide in preference to reacting with bromotrichloromethane which is present as solvent (eq. 26). The second, when steady state concentrations of the trichloromethyl radical react with steady state concentrations of hydrogen bromide in preference to much larger concentrations of toluene (eq. 26).

4) Walling and Mintz have shown that ethylene oxide is almost ten times more reactive than toluene toward *t*-butyl hypochlorite at 0°C.[39] This tendency for ethylene oxide to react as a hydrogen atom donor in the presence of electrophilic radicals may play a hidden role its effect on bromotrichloromethane selectivities. That it functions solely as a hydrogen bromide trap in the presence of both bromine atom and trichloromethyl radical seems unlikely.

5) Several studies have shown that an identity reaction may be important in reactions involving benzyl radicals (eq. 27).[40-42] Identity reactions of this type could be involved in deuterium scrambling.

$$ArCH_2\cdot + ArCH_2\text{-}H \rightleftharpoons ArCH_2\text{-}H + ArCH_2\cdot \qquad (27)$$

The above concerns and questions formed the impetus for our reinvestigation of the mechanism of photoinitiated benzylic bromination with bromotrichloromethane. We envisioned three experimental approaches toward answering the questions raised above.

Firstly, we felt that it was imperative that a rho value for reaction of the trichloromethyl radical with substituted toluenes be determined in an unambiguous fashion. Should this unambiguous rho value be identical to that obtained by Huyser, it

would suggest that the trichloromethyl radical was in fact the chain propagating species, and that the observations of Tanner and co-workers were caused by the radical reactivity of the ethylene oxide. Alternatively, similarity between an unambiguous rho value and that obtained by Tanner when additives were present would confirm the need for reconsideration of the Huyser mechanism.

Secondly, we felt that a systematic investigation of the free radical chemistry of epoxides would provide evidence for better understanding the effects observed in the presence of ethylene oxide. The literature contains only a few isolated reports of radical reactions involving epoxides.[39,43-45] In each of these cases, however, electrophilic radicals including *t*-BuO·,[39,43] Br·,[44] and Cl·[45] have led to the abstraction of hydrogen atoms from carbon atoms of the epoxide ring.

Thirdly, we felt an investigation of the possible role of the identity reaction under the bromination conditions used was in order. If it were found to be operative to a measurable degree, then its importance in the observation of deuterium scrambling should be ascertained. Results, which will be presented, made this part of the study unnecessary.

Results and Discussion

Initial attempts to generate the trichloromethyl radical in an unambiguous fashion were unsuccessful. Trichloroiodomethane was considered to be a suitable precursor for this radical. Haszeldine has reported its successful use in radical addition to 3,3,3-trifluoropropyne (eq. 28).[46] Trichloroiodomethane should be preparable by

$$Cl_3C\text{-}I \quad + \quad HC{\equiv}CCF_3 \xrightarrow[\text{or heat}]{h\nu} Cl_3CH{=}ClCF_3 \qquad (28)$$

treating bromotrichloromethane with sodium iodide in acetone (eq. 29). Precipitation of sodium bromide was observed, however attempts to isolate the $ICCl_3$ by distillation at reduced pressure failed due to decomposition of the material as evidenced by formation of I_2 and hexachloroethane (eq. 30). The lability of the carbon-iodine bond,

$$Br\text{-}CCl_3 \quad + \quad NaI \xrightarrow{\text{acetone}} I\text{-}CCl_3 \quad + \quad NaBr\downarrow \qquad (29)$$

$$I\text{-}CCl_3 \longrightarrow I_2 \quad + \quad Cl_3C\text{-}CCl_3 \qquad (30)$$

even at room temperature made $ICCl_3$ useless as a source of trichloromethyl radicals.

Another possible method of trichloromethyl radical generation is *via* the trichloroacetoxyl radical, which rapidly decarboxylates (eq. 31).[47] Three precursors of

$$Cl_3CCO_2\cdot \longrightarrow CO_2\uparrow \quad + \quad Cl_3C\cdot \qquad (31)$$

the trichloroacetoxyl radical were prepared. The first was trichloroacetyl peroxide. This was synthesized by treating trichloroacetyl chloride with sodium peroxide.[48]

Observations by Leffler and Gibson that "the peroxide has a half-life of about 10 minutes in solutions at 0° and the solid explodes at room temperature,"[49] were loosely confirmed. It proved to be too unstable to be used as a source of trichloromethyl radical for benzylic hydrogen abstraction.

t-Butyl trichloroperacetate was prepared by treating trichloroacetyl chloride with *t*-butyl hydroperoxide and pyridine.[49] The perester is considerably more stable than either trichloroiodomethane or trichloroacetyl peroxide. Scheme 8 shows the expected mechanistic steps involved in the decomposition of the perester in the presence of a substituted toluene. Experiments in which the perester was decomposed

$$Cl_3CO_2\text{-}OC(CH_3)_3 \longrightarrow Cl_3C\cdot + (CH_3)CO\cdot + CO_2\uparrow \quad (32)$$

$$Cl_3C\cdot + ArCH_2\text{-}H \longrightarrow H\text{-}CCl_3 + ArCH_2\cdot \quad (22)$$

$$(CH_3)CO\cdot + ArCH_2\text{-}H \longrightarrow (CH_3)_3CO\text{-}H + ArCH_2\cdot \quad (33)$$

$$(CH_3)CO\cdot \longrightarrow CH_3C(O)CH_3 + CH_3\cdot \quad (34)$$

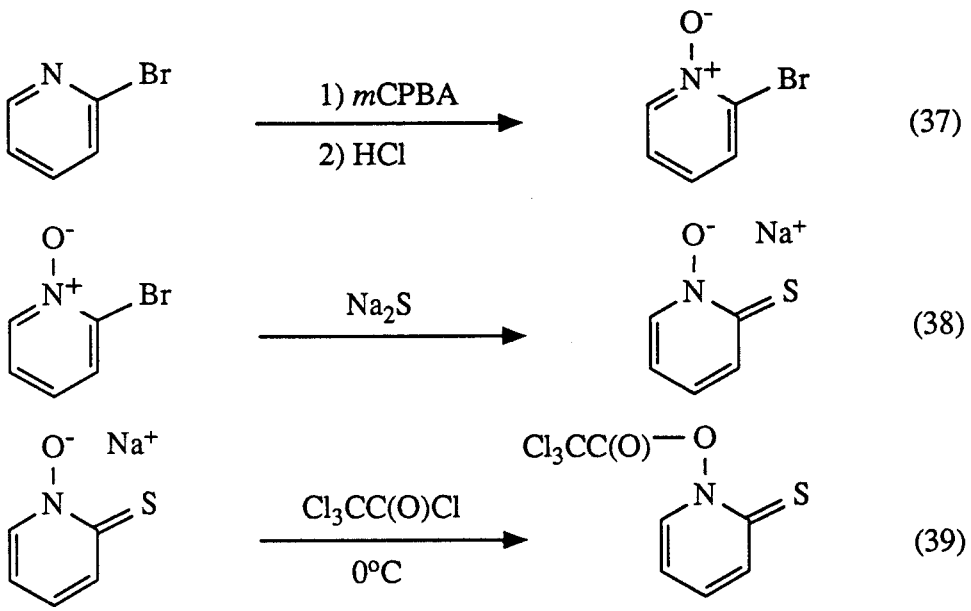
$$2\ Cl_3C\cdot \longrightarrow Cl_3C\text{-}CCl_3 \quad (35)$$

$$2\ ArCH_2\cdot \longrightarrow ArCH_2\text{-}CH_2Ar \quad (36)$$

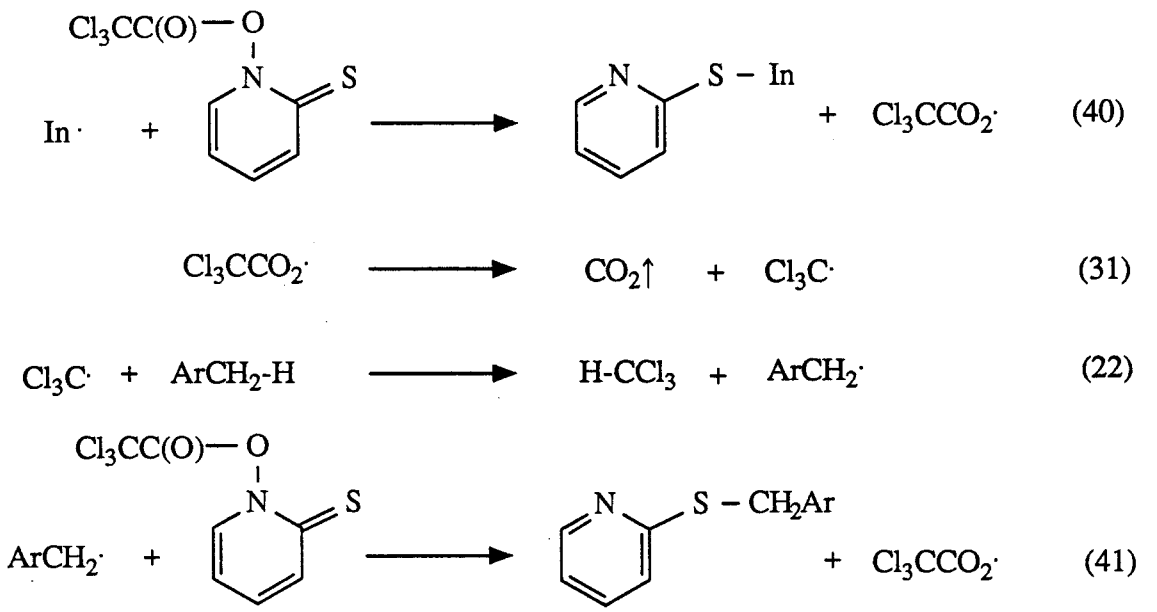
Scheme 8. Expected mechanism for reaction of *t*-butyl trichloroperacetate with substituted toluenes.

in an excess of toluene or *p*-xylene at 70° for several days showed large variation between like runs. Concentrations of chloroform were especially difficult to analyze by capillary GC and varied by as much as 30%. The problems associated with GC analysis are apparently due to decomposition of unreacted perester in the injection port. However, even after extensive reaction times (11 days), the same difficulties remained. It was felt that other methods of trichloromethyl radical generation should be pursued.

The final approach to generating the trichloroacetoxyl radical was based on methodology developed by Barton.[50-52] Preparation of the necessary thiohydroxamic ester was envisioned *via* the series of steps shown in scheme 9.[52, 53] The expected chain mechanism for the reaction of the thiohydroxamic ester with a substituted toluene is shown in Scheme 10. Barton and co-workers have successfully extended this approach

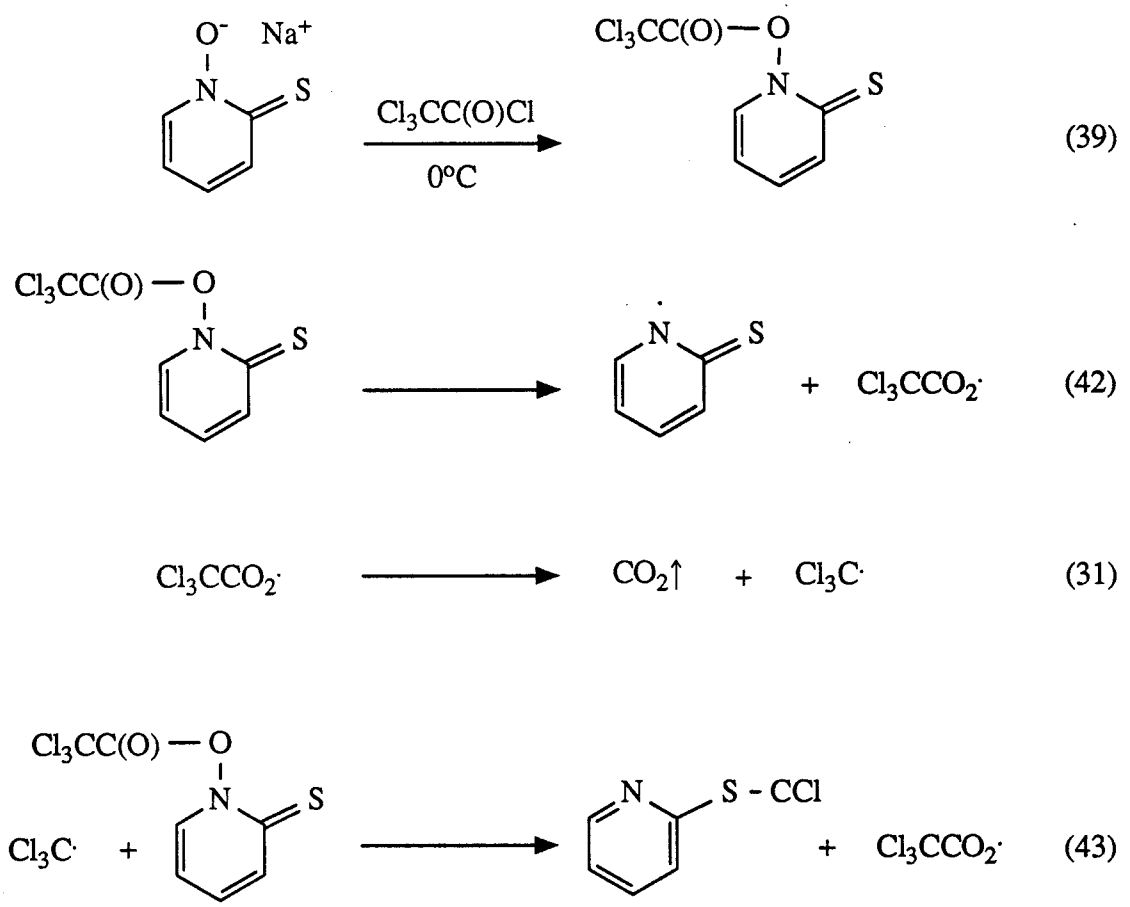


Scheme 9. Synthesis of "Barton" type radical precursor.



Scheme 10. Expected chain mechanism for "Barton" radical precursor.

to include the generation of trifluoromethyl radicals,[54] however attempts at preparing trichloromethyl radicals in this manner failed. In the last step of the proposed synthesis (eq. 39), addition of trichloroacetyl chloride to a solution containing pyridine-2-thione-N-oxide at 0°, rapid evolution of gas was observed. No chloroform, or hexachloroethane was observed when the addition was carried out in the presence of cumene. Apparently, decomposition of the reaction product occurs rapidly in the fashion outlined in scheme 11.



Scheme 11. Possible route of observed decomposition of the "Barton" radical precursor.

Minisci and co-workers have shown that methyl radicals can be conveniently generated from acetone and hydrogen peroxide (Scheme 12).[55] An extension of the

$$2\ CH_3C(O)CH_3 + HOOH \longrightarrow (CH_3)_2C(OH)\text{-}O\text{-}O\text{-}(HO)C(CH_3)_2 \quad (44)$$

$$(CH_3)_2C(OH)\text{-}O\text{-}O\text{-}(HO)C(CH_3)_2 \longrightarrow 2\ (CH_3)_2C(OH)\text{-}O\cdot \quad (45)$$

$$(CH_3)_2C(OH)\text{-}O\cdot \longrightarrow CH_3\cdot + CH_3CO_2H \quad (46)$$

Scheme 12. Generation of methyl radicals from acetone and hydrogen peroxide.

methodology, in order to generate trichloromethyl radicals was attempted. Treatment of hexachloroacetone with aqueous hydrogen peroxide generated chloroform and trichloroacetic acid. Unfortunately, a control experiment showed the same products in the absence of hydrogen peroxide. Hydrolysis of hexachloroacetone is evidently occurring independent of the hydrogen peroxide (Scheme 13). The trichloromethyl anion is a reasonable leaving group, based on analogy with its behavior in the haloform reaction of methylketones.[56]

$$Cl_3CC(O)CCl_3 + H_2O \longrightarrow (Cl_3C)_2C(OH)_2 \quad (47)$$

$$(Cl_3C)_2C(OH)_2 \longrightarrow H\text{-}CCl_3 + Cl_3CCO_2\text{-}H \quad (48)$$

Scheme 13. Hydrolysis of hexachloroacetone.

It was eventually decided to shift attention from attempts to develop new precursors, toward carrying out the same benzylic brominations with bromotrichloromethane under conditions in which only the trichloromethyl radical may be operative. The ambiguity in the identity of the chain propagating species arises from the generation of two different radicals in the initiation step (eq. 19). Alternative methods of initiation should be free from this complication. Thermal decomposition of

azobisisobutyronitrile (AIBN) is a commonly used method of radical generation.[57] When AIBN is used in brominations with bromotrichloromethane, it initiates a chain process that involves only the trichloromethyl radical and is free of bromine atom participation (Scheme 14).

$$((CH_3)_2C(CN)\text{-}N{=})_2 \longrightarrow 2\ (CH_3)C(CN)\cdot + N_2\uparrow \quad (49)$$

$$(CH_3)C(CN)\cdot + BrCCl_3 \longrightarrow (CH_3)C(CN)\text{-}Br + Cl_3C\cdot \quad (50)$$

$$ArCH_2\text{-}H + Cl_3C\cdot \longrightarrow ArCH_2\cdot + HCCl_3 \quad (22)$$

$$ArCH_2\cdot + BrCCl_3 \longrightarrow ArCH_2Br + Cl_3C\cdot \quad (23)$$

Scheme 14. Mechanism for thermal initiated benzylic bromination by $BrCCl_3$.

Relative rates of reaction for pairs of toluenes have been studied for AIBN initiated bromination with bromotrichloromethane. The long half-life of AIBN at 50° necessitated the use of a higher temperature (70°). This modification did not allow for a direct comparison of results with those of Huyser[28] or Tanner *et al.*[31] For this reason, relative reactivities of substituted toluenes under photoinitiated bromination conditions with bromotrichloromethane at 70° were determined. In order to allow comparison of these methods with results for bromine atom propagation, photoinitiated brominations with NBS were also reinvestigated at 70°. In each case, relative reactivities were determined for pairs of substituted toluenes by direct competition. Relative concentrations of the two substrates, bromotrichloromethane, and internal standard were approximately 1 : 1 : 15 : 0.5. The reactions were carried out in a nitrogen atmosphere at reduced pressure in sealed pyrex ampules. Reactions were run to at least 10% consumption of the less reactive substrate as determined by GC. Tables 8, 9, and 10 contain the relative reactivities, of the substrates studied, for benzylic brominations by AIBN initiation of bromotrichloromethane, photoinitiation of bromotrichloro-

methane, and photoinitiation of NBS respectively. It may be noted that toluene itself does not appear in any of the studies. This is due to difficulties encountered in resolving toluene and bromotrichloromethane under the GC conditions employed.

Table 8. Relative rates of reaction for substituted toluenes with $BrCCl_3$ at 70°, initiated with AIBN.

Substrate	Number of runs	Rate relative to *p*-xylene
p-methoxytoluene[a]	5	1.31 ± 0.13
p-xylene[b]	-	1.00
p-*tert*-butyltoluene	5	0.97 ± 0.06
m-xylene[b,c]	5	0.69 ± 0.03
p-chlorotoluene	4	0.68 ± 0.06
m-chlorotoluene	5	0.45 ± 0.01
m-trifluoromethyltoluene[c]	4	0.48 ± 0.10
p-cyanotoluene[c]	5	0.35 ± 0.07
3,5-dibromotoluene[c]	5	0.41 ± 0.02

a) Corrected for reaction at the ether methyl group.
b) Statistically corrected.
c) Run relative to *p*-chlorotoluene.

Table 9. Relative rates of reaction for substituted toluenes with $BrCCl_3$ at 70°, photoinitiated.

Substrate	Number of runs	Rate relative to *p*-xylene
p-methoxytoluene[a]	6	2.10 ± 0.06
p-xylene[b]	-	1.00
p-*tert*-butyltoluene	6	0.96 ± 0.05
m-xylene[b,c]	4	0.55 ± 0.04
p-chlorotoluene	5	0.54 ± 0.05
m-chlorotoluene	6	0.42 ± 0.04
m-trifluoromethyltoluene[c]	4	0.24 ± 0.03
p-cyanotoluene[c]	4	0.12 ± 0.01
3,5-dibromotoluene[c]	5	0.28 ± 0.01

a) Corrected for reaction at the ether methyl group.
b) Statistically corrected.
c) Run relative to *p*-chlorotoluene.

Table 10. Relative rates of reaction for substituted toluenes with NBS at 70°, photoinitiated.

Substrate	Number of runs	Rate relative to *p*-xylene
p-methoxytoluene	4	3.88 ± 0.33
p-xylene[a]	-	1.00
p-*tert*-butyltoluene	5	1.05 ± 0.04
m-xylene[a,b]	5	0.62 ± 0.09
p-chlorotoluene	4	0.41 ± 0.05
m-chlorotoluene	5	0.10 ± 0.02
m-trifluoromethyltoluene[b]	4	0.09 ± 0.02
p-cyanotoluene[b]	6	0.13 ± 0.02
3,5-dibromotoluene[b]	5	0.06 ± 0.01

a) Statistically corrected.
b) Run relative to *p*-chlorotoluene.

Hammett correlations with sigma and sigma-plus constants for each set of reaction conditions were performed (Table 11). In each case, optimum correlation was obtained when sigma-plus constants were used (Figures 3, 4, and 5). This is expected based on the electrophilic nature of each of the potential hydrogen abstracting radicals.[58] Table 11 also shows that the magnitude of the rho value is dependent on the method of bromination used.

Table 11. Comparison of rho values with method of benzylic bromination at 70°.

	Substituent constants	
Method	sigma (r^a)	sigma-plus (r^a)
$BrCCl_3$, AIBN	-0.58 (0.93)	-0.38 (0.98)
$BrCCl_3$, hv	-1.09 (0.92)	-0.70 (0.95)
NBS, hv	-1.68 (0.86)	-1.17 (0.97)

a) Correlation coefficient.

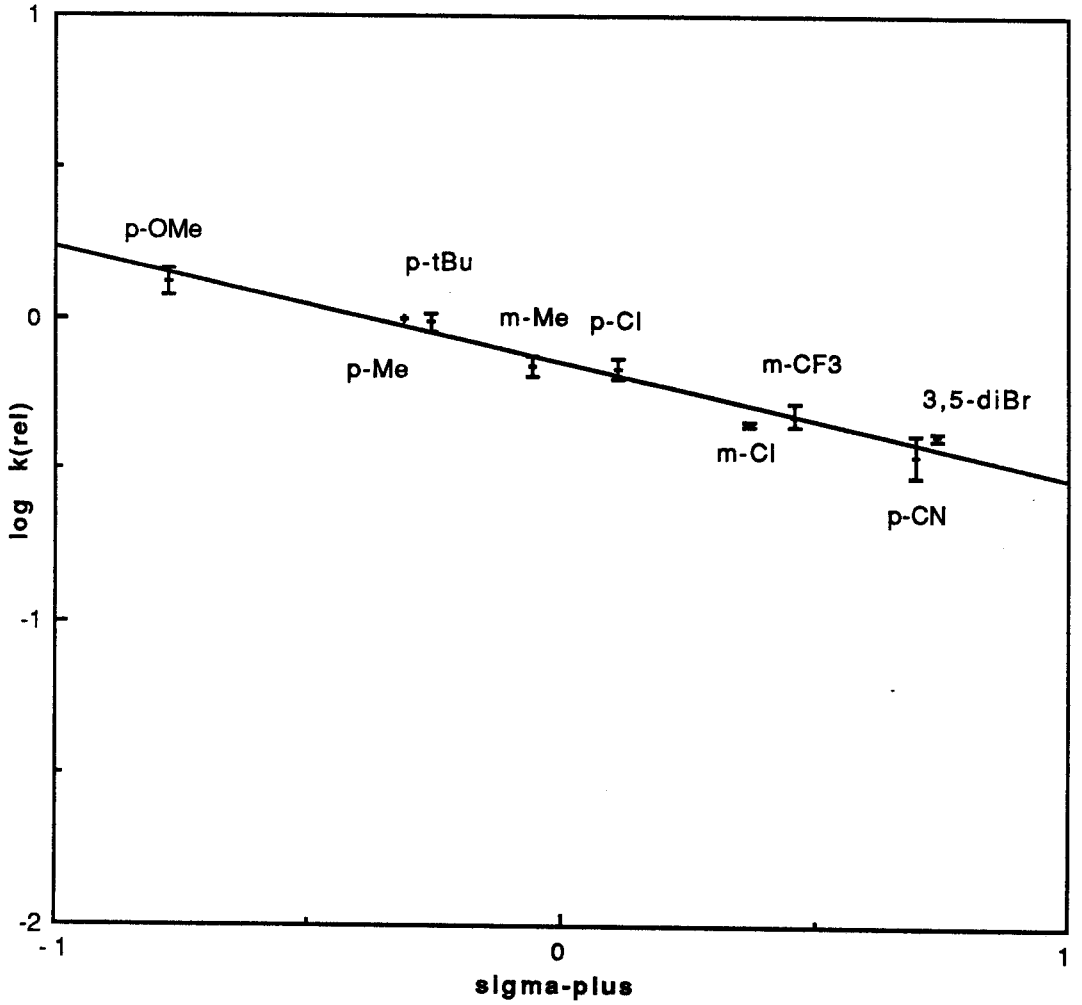


Figure 3. Hammett plot of the logs of the relative reactivities for the photoinitiated reactions of substituted toluenes with $BrCCl_3$ at 70° versus sigma-plus constants.

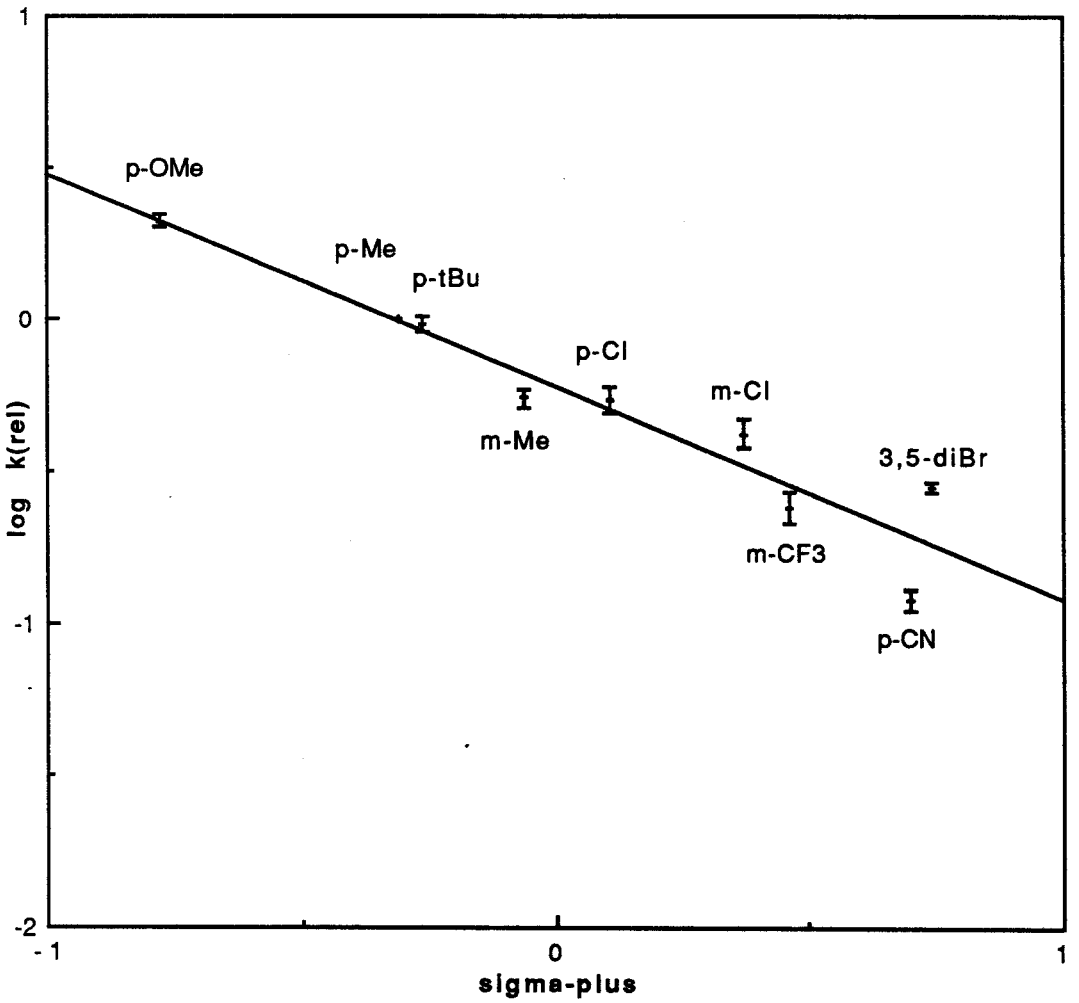


Figure 4. Hammett plot of the logs of the relative reactivities for AIBN initiated reactions of substituted toluenes with $BrCCl_3$ at 70° versus sigma-plus constants.

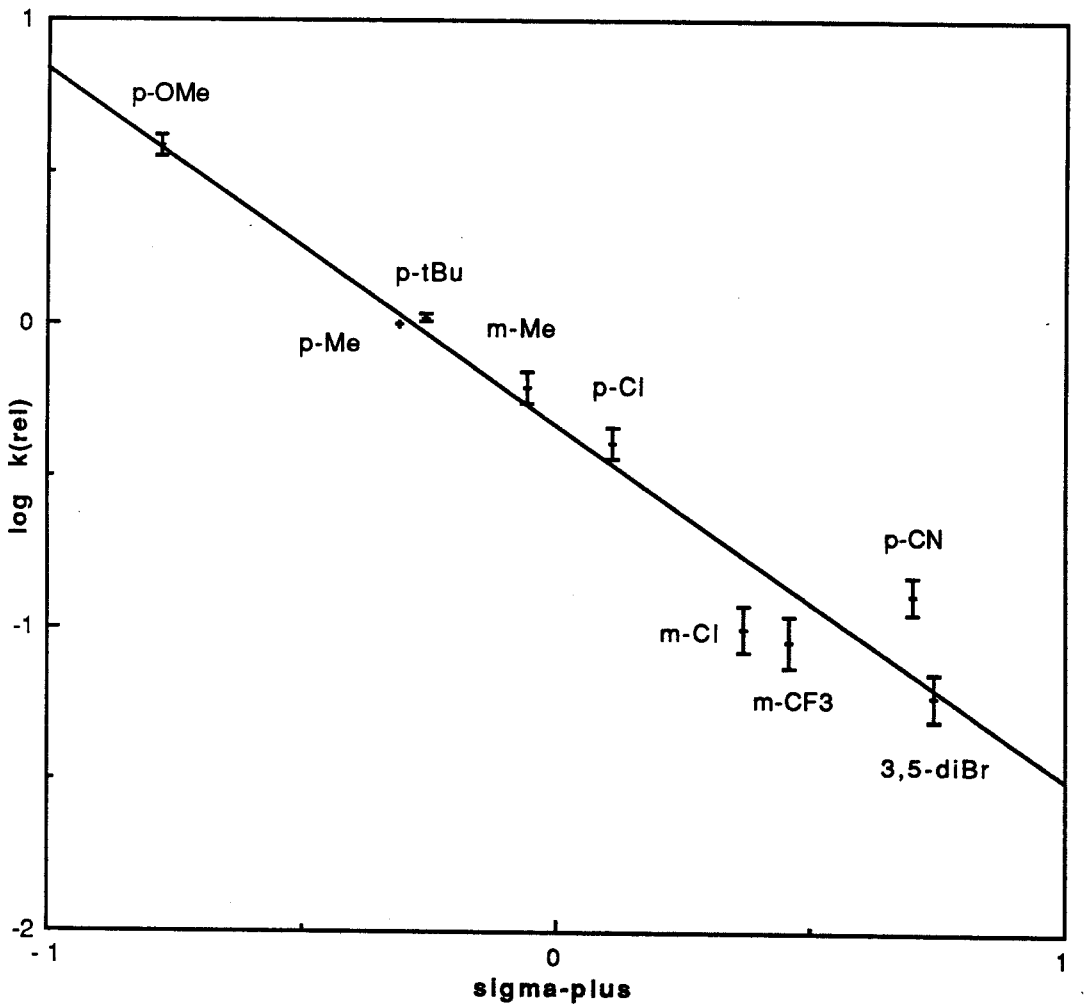


Figure 5. Hammett plot of the logs of the relative reactivities for photoinitiated reactions of substituted toluenes with NBS at 70° versus sigma-plus constants.

The AIBN initiated reactions of bromotrichloromethane demonstrate the least sensitivity to substituent variation with a rho value of only -0.38. Photoinitiated reactions of bromotrichloromethane show greater selectivity than their thermally initiated counterparts, with a rho value of -0.70. Still greater sensitivity to substituent variation is observed for brominations with NBS, and a rho value of -1.17 is obtained. This variation indicates that for the case of photoinitiated benzylic brominations with bromotrichloromethane, both the bromine atom and the trichloromethyl radical are involved in chain propagation. AIBN initiation effectively eliminates participation by the bromine atom, proving a good method for measuring relative reactivities which are due solely to the trichloromethyl radical. It has already been shown that bromination with NBS, is a suitable method for measuring the selectivities of the bromine atom.[16]

Since his initial reports, Tanner has suggested the possibility that bromine atom may not be the sole chain carrying radical in photoinitiated bromination with bromotrichloromethane.[59] With the above data, a semiquantitative estimate of the percentage of chain propagation which is due to each radical, in the photoinitiated case, can be made. Figure 6 shows a graphical correlation of rho values with method of bromination. This treatment of the data suggests that about 60% of the hydrogen abstractions are by the trichloromethyl radical and 40% are by the bromine atom.

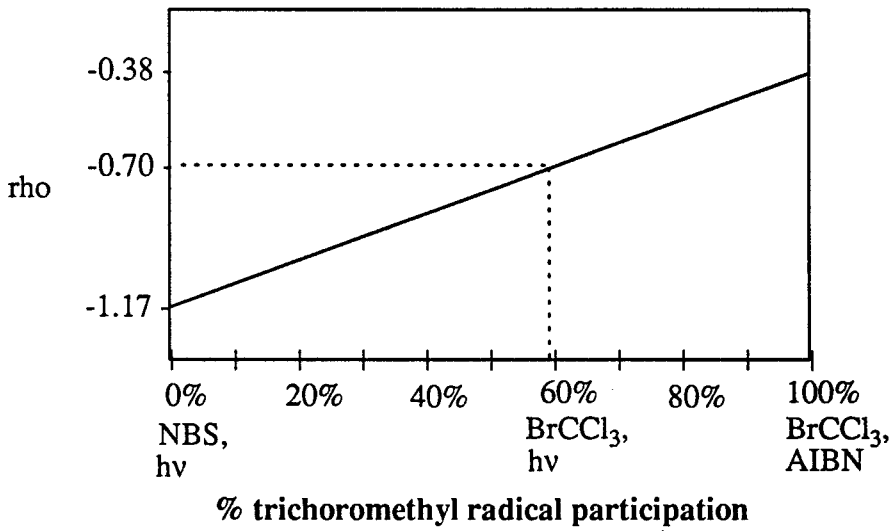


Figure 6. Estimation of the percent of chain propagation due to the trichloromethyl radical in photoinitiated brominations with $BrCCl_3$.

The rho values at 70° are in good agreement with the previously reported results at 50°,[28,31] when the temperature difference is considered. Although it was not practical to determine rho values at the lower temperature (due to the long half-life of AIBN), the relative reactivity for a single pair of substituted toluenes was determined at several temperatures under photoinitiated conditions. Table 12 contains the results of this investigation. The relative rate of reaction for *p*-methoxytoluene versus *p*-xylene

Table 12. Effect of temperature change on the relative rate of photoinitiated bromination by $BrCCl_3$ for *p*-methoxytoluene *vs.* *p*-xylene.

Temperature	Number of runs	k_{rel}
70°	6	2.39 ± 0.24
60°	5	2.62 ± 0.11
50°	5	2.79 ± 0.04
40°	4	2.95 ± 0.40

increases linearly (r=0.996) with decreasing temperature over a 30° range. This observed increase in selectivity at lower temperatures parallels the difference in rho values at 50 and 70°.

The partitioning of chain propagation between the bromine atom and the trichloromethyl radical is apparently insensitive to variation in chain length. This is evident from an investigation of the relative reactivities for a pair of substituted toluenes with varying concentrations of bromotrichloromethane, under conditions of photoinitiation. The same relative rate is obtained for reactions in which the bromotrichloromethane is present in a sixteen fold excess as for reactions in which it is present as the limiting reagent (Table 13).

Table 13. Effect of $BrCCl_3$ concentration on the relative rate of photoinitiated bromination by $BrCCl_3$ for *p*-methoxytoluene *vs.* *p*-xylene at 70°.

$BrCCl_3$: *p*-methoxytoluene : *p*-xylene	Number of runs	k_{rel}
16 : 1 : 1	5	2.39 ± 0.04
10 : 1 : 1	6	2.39 ± 0.24
4 : 1 : 1 [a]	5	2.36 ± 0.08
1 : 1 : 1 [a]	8	2.36 ± 0.13
0.5 : 1 : 1 [a]	6	2.39 ± 0.14

a) Concentrations of substrates maintained by adding CH_2Cl_2.

A reinvestigation of every study ever done on the trichloromethyl radical, using thermal initiation (no matter how entertaining that might be) seemed impractical. The small ρ^+ value obtained for the trichloromethyl radical indicates, as Tanner first suggested,[31] that this radical is less sensitive to electronic variation than was originally believed based on photoinitiated reactions of bromotrichloromethane. Its sensitivity, however, to steric hindrance at the reaction site seemed to be an issue meriting some reexamination.

Francisco has investigated the geometry of the trichloromethyl radical by *ab initio* calculations at the 3-21 G and 6-31 G* levels (Figure 7).[60]

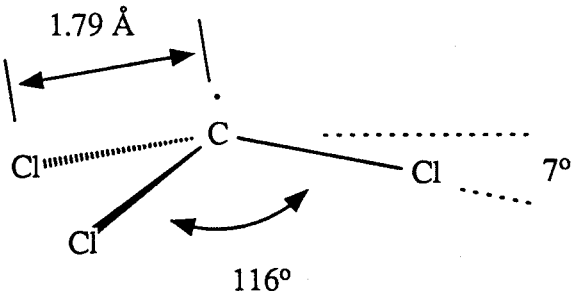


Figure 7. Geometry of the trichloromethyl radical based on *ab initio* calculations (reference 60).

His results are in excellent agreement with an experimental value of the bond angle (116°) which was obtained, *via* ESR, by Hesse.[61] The pyramidyl shape of the radical and its larger size compared to a bromine atom could give rise to a greater sensitivity to steric effects.

Eghdami, Gleicher, and Totherow have reported the relative rates of reaction of a series of unsubstituted alkylbenzenes with bromotrichloromethane.[62] They found a decrease in reactivity as the size of the alkyl groups increased (Table 14). They interpreted these results in terms of steric effects on the trichloromethyl radical. Because their study utilized photoinitiation, however, the extent to which the smaller bromine atom participates in hydrogen abstraction is unclear. In order to determine more specifically the sensitivity of the trichloromethyl radical to steric changes, a reinvestigation of this study was carried out.

Table 15 contains the results of AIBN initiated reactions of bromotrichloromethane with unsubstituted alkylbenzenes at 70°. These reactions were run as a direct competition of pairs of alkylbenzenes, in a manner identical with that

used for the substituted toluenes. In each case, relative reactivities are reported on a per hydrogen basis.

Table 14. Relative rates for photoinitiated reactions of unsubstituted alkylbenzenes with $BrCCl_3$ at 70°.[a]

Substrate	k_{rel}[b]
cumene	6.49 ± 0.20
sec-butylbenzene	3.12 ± 0.13
3-phenylpentane	1.10 ± 0.13
ethylbenzene	1.00
n-propylbenzene	0.79 ± 0.06
isobutylbenzene	0.27 ± 0.01
neopentylbenzene	0.02 ± 0.004

a) Taken from reference 62.
b) All results statistically corrected for number of benzylic hydrogen atoms.

Table 15. Relative rates for AIBN initiated reactions of unsubstituted alkylbenzenes with $BrCCl_3$ at 70°.

Substrate	Number of runs	k_{rel}[a]
cumene	4	4.51 ± 0.24
sec-butylbenzene	5	2.02 ± 0.08
3-phenylpentane	6	0.57 ± 0.03
ethylbenzene	-	1.00
n-propylbenzene	6	0.61 ± 0.02
isobutylbenzene	6	0.43 ± 0.03
neopentylbenzene	6[b]	< 0.006

a) All results statistically corrected for number of benzylic hydrogens.
b) Upper limit of the reactivity based on a single run, the other five runs showed no reaction of the neopentylbenzene.

Changes in the magnitudes of the relative rates were again observed as a result of AIBN initiation. A decrease in the relative rate of cumene to ethylbenzene was observed upon elimination of bromine atom participation. This decrease in selectivity agrees well with a similar result observed in the presence ethylene oxide or potassium carbonate (see Table 6).[32] These observations are consistent with the smaller sensitivity to electronic variation of the trichloromethyl radical compared to the bromine atom. A different trend is seen for comparisons made within sets of secondary and tertiary alkylbenzenes.

For AIBN initiated reactions, 3-phenylpentane is only about half as reactive as ethylbenzene, even though the former is a tertiary compound and the latter is a secondary compound. Perhaps a more accurate estimation of the importance of steric

effects can be made by comparing the relative rates of reaction for cumene : 3-phenylpentane. When reactions are photoinitiated, this ratio is 5.90. Its value increases to 7.91, when AIBN is used. This represents a 34% increase in selectivity favoring the less hindered substrate, when bromine atom participation is removed.

Similar differences are observed for secondary substrates. Neopentylbenzene showed no measurable reaction after 240 hours. An estimate of the upper limit for the relative reactivity of neopentylbenzene of 0.006 relative to ethylbenzene, suggests that this compound is at least three times less reactive when AIBN initiation is used.

The above results demonstrate the nature of the reactivity of the trichloromethyl radical. Most notably, it is less sensitive toward electronic changes in the substrate, and more sensitive toward steric changes than photoinitiated reactions indicate.

Recently, a group of Soviet workers has published an article that is related to the above findings.[63] This article reports the results of reactions of bromotrichloromethane with toluene, initiated with AIBN in the presence and absence of ethylene oxide. Based on the observation of 2-bromoethanol in the latter reaction, this group has suggested that bromine atom participation is necessarily involved in hydrogen atom abstraction, *even in the reactions initiated with AIBN*. They did not propose a mechanism for the generation of bromine atoms, nor did they investigate any reactivity changes due to the change of initiation method. This report should be viewed with skepticism. In light of the consistent and sometimes dramatic differences in reactivity for the reactions initiated by AIBN, it is clear that the bromine atom cannot participate to as great a degree as it does in photoinitiated reactions. Furthermore, reactivity changes for compounds such as 3-phenylpentane, and neopentylbenzene make a model involving bromine participation in thermally initiated reactions difficult to accept.

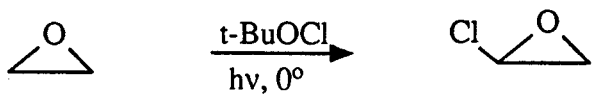
Part II. Chlorine Atom Abstractions from α- and β-Chloroepoxides by the Triphenyltin Radical.

Discussion of the Problem

The use of ethylene oxide as a hydrogen bromide trapping agent in brominations with bromotrichloromethane, and its effect on the selectivity of those reactions have been discussed above. The possibility that radicals generated from ethylene oxide might be involved in chain propagation and selectivity changes, was considered. The results presented in Part I are consistent with the original description of ethylene oxide acting solely as a hydrogen bromide trap. However, the literature on the subject of radical reactions of epoxides is both sparse and sometimes contradictory. While about thirty papers (over the course of as many years) have appeared, they serve only to address a wide variety of reactions without attention to reactivity trends for epoxides of differing structure. It was felt that an investigation of certain radical reactions of epoxides would be an important contribution to the understanding of the behavior of this functional group, despite its lessened relevance to the original investigation of benzylic brominations.

Radical chemistry of epoxides can be divided into two major categories based on the relationship between the radical site and the epoxide ring. If the radical site is at one of the carbons of the epoxide itself, the species is termed an α-epoxy radical. On the other hand, if the radical is located at an exocyclic carbon, then the species is referred to as a β-epoxy radical. The following discussion of the literature will summarize the studies that have appeared concerning both α- and β-epoxy radicals.

The generation of α-epoxy radicals has been accomplished, most often, by hydrogen atom abstraction from an epoxide by an electrophilic radical. Walling's group was among the first to report this type of reaction.[64] They used *t*-butyl hypochlorite to chlorinate ethylene oxide and propylene oxide at 0°, the main products were the corresponding α-chloroepoxides (eqs. 51 and 52). In a later paper the relative



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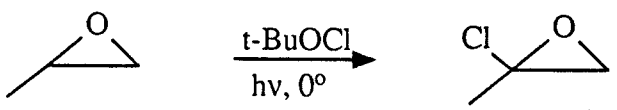


(52)

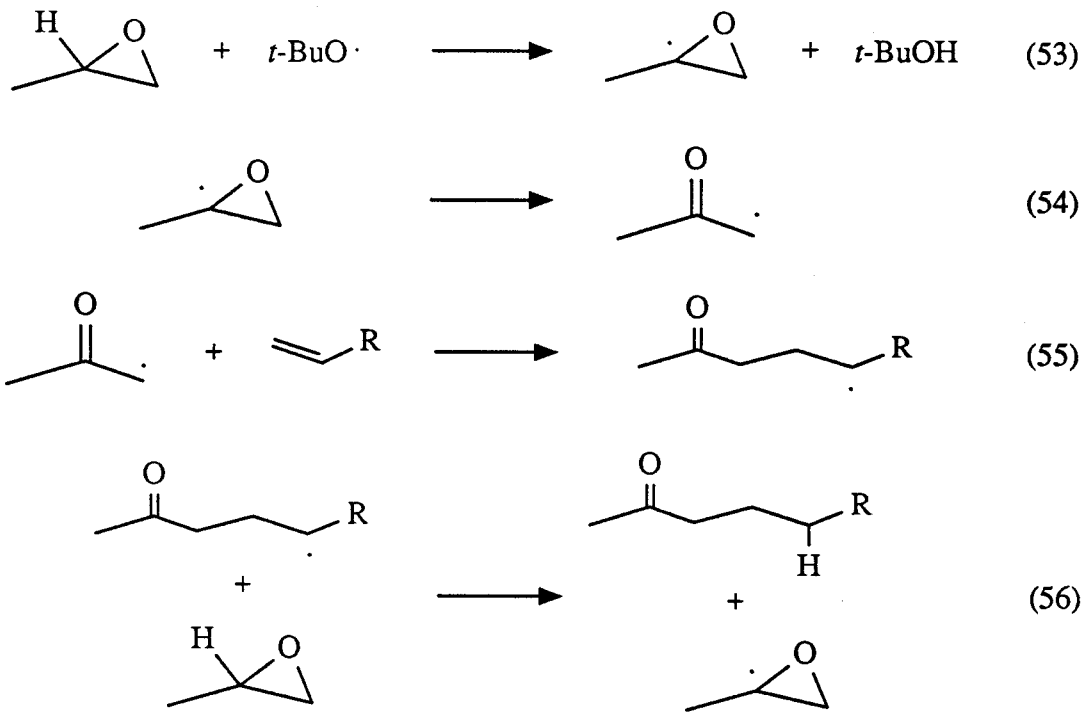
rates of reaction for a large number of compounds, including four epoxides and toluene were reported (Table 16).[39] This one paper represents the entire body of work addressing the question of relative reactivities for radical generation in epoxides.

Table 16. Relative rates of photoinitiated reaction for several epoxides with *t*-BuOCl at 0°.[a]

Substrate	Relative rates of disappearence.	Relative rates per hydrogen.
propylene oxide	33.6	100.8
ethylene oxide	13.1	9.8
toluene	1.00	1.0
styrene oxide	0.24	0.7
isobutylene oxide	0.20	0.3

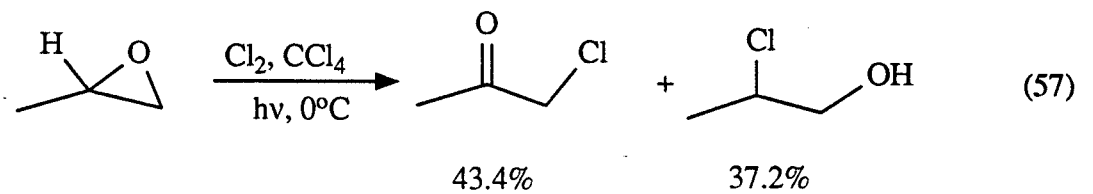
a) Reference 39.

Other examples of hydrogen atom abstraction from epoxides by electrophilic radicals include studies by Wallace and Gritter,[65] Etlis *et al.*,[45] and Calò *et al.*[44] In each case, only ring opened products were observed. Wallace and Gritter first reported rearrangement of an α-epoxy radical to an α-keto radical in the reactions of propylene oxide with 1-octene initiated with *t*-butyl peroxide at 125-150° (Scheme 15).[65] Etlis



Scheme 15. Mechanism for formation of 1:1 adducts of propylene oxide and terminal olefins, initiated with *t*-butyl peroxide at 150°.[65]

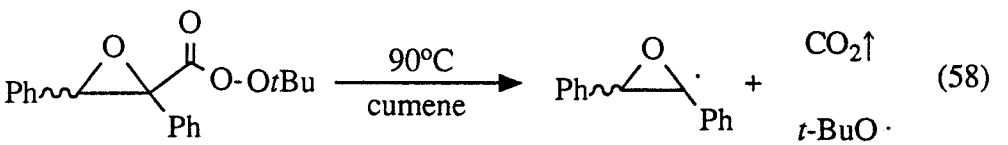
and co-workers studied the photoinitiated chlorination of ethylene oxide and propylene oxide with molecular chlorine at low temperatures.[45] For the case of propylene oxide, the major products were chloroacetone and propylene chlorohydrin (eq. 57). The



formation of chloroacetone was rationalized by rearrangement of the epoxy radical (eq. 54), followed by chlorine atom abstraction from molecular chlorine. Calò and co-workers have reported excellent yields of bromomethylketones (85-90%) from the photoinitiated reactions of terminal epoxides and molecular bromine at room temperature.[44] They also invoke equation 54 in their proposed mechanism. In addition, they observed no bromohydrins despite the generation of an equivalent of hydrogen bromide during the reaction.

Several other aspects of α-epoxy radicals have been investigated. They specifically include: the pyramidyl geometry of the radical, the rate and mechanism of inversion, and the rate of rearrangement to α-carbonyl radicals.

The first study that attempted to ascertain the geometry of α-epoxy radicals was carried out by Padwa and Das.[66] They attempted to determine the existence of stereochemical "memory" in the decomposition of *t*-butyl *cis*- and *trans*-α,β-diphenylperglycidates in cumene (eq. 58). For either isomer, about 20% of



(58)

the α-epoxy radicals generated were trapped as *trans*-stilbene oxide, while the other 80% rearranged to the corresponding α-keto radicals and gave ketone products. The same products in the same ratios were observed for each diastereomer. This indicates complete equilibration of the radicals had occurred.

Altman and Baldwin have successfully demonstrated the ability of α-epoxy radicals to retain their geometry in the presence of better chain transfer agents. Their results are summarized in Equations 59 and 60 as well as Table 17.[43] They found that

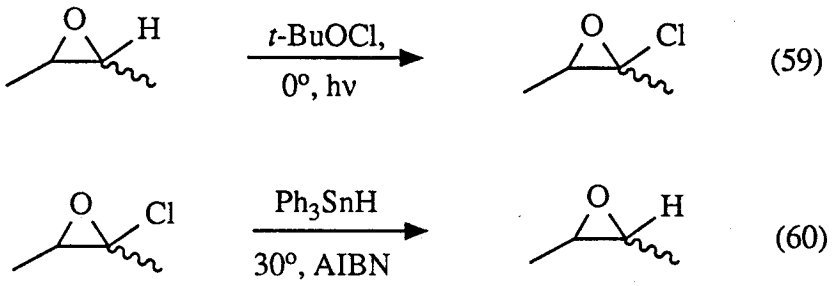


Table 17. Stereochemical integrity of α-epoxy radicals generated by hydrogen or chlorine atom abstraction at 0 or 30° respectively.[a]

Starting material	Reaction conditions	Product Ratio *cis* : *trans*
cis-2,3-epoxybutane	*t*-BuOCl, 0°, hv	98.5 : 1.5 [b]
trans-2,3-epoxybutane	*t*-BuOCl, 0°, hv	1.5 : 98.5 [b]
cis-2-chloro-2,3-epoxybutane	Ph_3SnH, 30°, AIBN	55.0 : 45.0 [c]
trans-2-chloro-2,3-epoxybutane	Ph_3SnH, 30°, AIBN	8.0 : 92.0 [c]

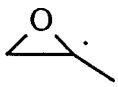
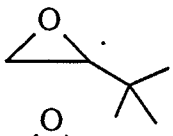
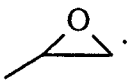
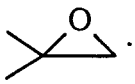
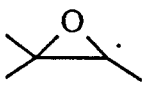
a) Reference 43.
b) Product is 2-chloro-2,3-epoxybutane.
c) Product is 2,3-epoxybutane.

chlorination of *cis*- or *trans*-2,3-epoxybutane with *t*-butyl hypochlorite at 0° gave the corresponding 2-chloro-2,3-epoxybutanes with almost complete retention of starting geometry. Reduction of the *cis*- or *trans*-2-chloro-2,3-epoxybutanes with triphenyltin hydride at 30° also showed some "memory" of starting geometry. The rate constant for

inversion was determined to be 1.1 x 10^7 sec^{-1}. It was also estimated that, based on these results, *t*-butyl hypochlorite is approximately 100 times more efficient than triphenyltin hydride as an atom transfer agent.

Electron spin resonance (ESR) has been used on several occasions to investigate both inversion and rearrangement of α-epoxy radicals.[67-69] Behrens and Schulte-Frohlinde were the first to observe and identify an α-epoxy radical by ESR.[67] An ESR spectrum, consistent with a pyramidyl radical shape was observed. The most complete treatment of α-epoxy radicals by ESR is that of Itzel and Fischer.[68] Their twenty-one page paper contains measured rates for the inversion and rearrangement of seven different α-epoxy radicals (Table 18). Recently, Ingold *et al.* have measured

Table 18. Temperatures at which inversion and rearrangement equal 10^7 sec^{-1} and 10^3 sec^{-1} respectively as measured by ESR.[a]

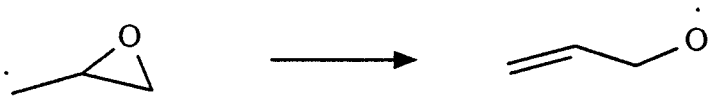
Radical	T_i (°C)[b]	T_r (°C)[c]
	-180 ± 20	> 70
	< -100	0 ± 5
	> -50	-30 ± 5
	-110 ± 10	> 0
	-55 ± 5	-35 ± 5
	-80 ± 5	-10 ± 10
	-15 ± 5	-45 ± 5

a) Reference 68.
b) T_i is the temperature at which the rate constant for inversion is approximately equal to 1 x 10^7.
c) T_r is the temperature at which the rate constant for rearrangement is approximately equal to 1 x 10^3.

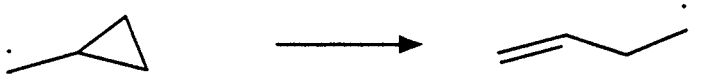
kinetic isotope effects for the inversion process and suggest that it involves quantum mechanical tunneling.[69] A theoretical analysis of the rearrangement and inversion processes has also recently appeared.[70] Semi-empirical molecular orbital calculations (MINDO/3) were used to evaluate the effects of substitution on these processes in

terms of the frontier molecular orbitals.[70]

The first report of β-epoxy radicals is due to Sabatino and Gritter.[71] They showed that at 150° *t*-butoxyl radicals, generated using *t*-butyl peroxide will abstract hydrogen atoms from both the α- and β-positions of cyclohexene oxide. From the relative amounts of cyclohexanone (α-H abstraction), cyclohexenone (β-H abstraction), and cyclohexenol (β-H abstraction) reported, it can be estimated that abstraction of an α-hydrogen atom occurs about 4 times faster than abstraction of a β-hydrogen atom. The nature of the products can be rationalized based on a ring opening rearrangement (eq. 61) which is completely analogous to that observed for cyclopropyl carbinyl (eq. 62).[72] Ring opening rearrangement is sufficiently rapid that no case of spectroscopic



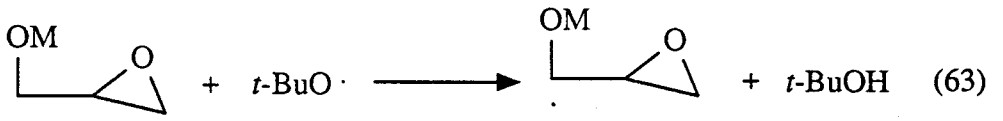
(61)



(62)

observation or chemical trapping of unrearranged β-epoxy radicals has been reported, *vida infra.*

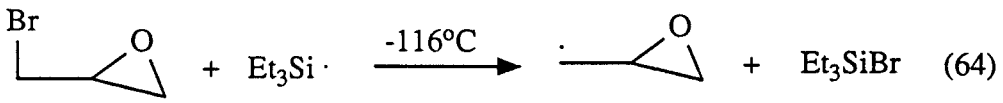
Davies *et al.* have had success in generating β-epoxy radicals by hydrogen atom abstraction from the β-position of glycidols and their ethers with *t*-butoxyl radicals (eq. 63).[73-75] ESR studies of radicals generated in this manner have failed to show signals



(63)

M = H, Me, Bu_3Sn, Me_3Si

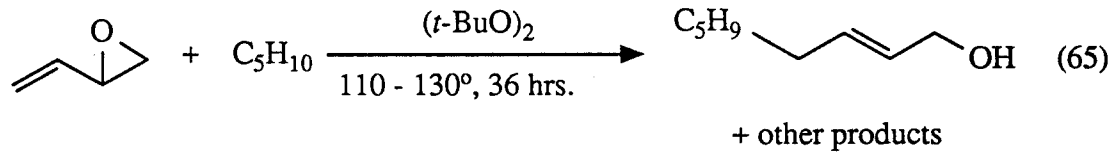
due to unrearranged β-epoxy radicals, even at temperatures as low as -100°. Davies has also generated the simplest β-epoxy radical, 2,3-epoxy-1-propyl, by treatment of epibromohydrin (1-bromo-2,3-epoxypropane) with triethylsilyl radicals (eq. 64).[73]



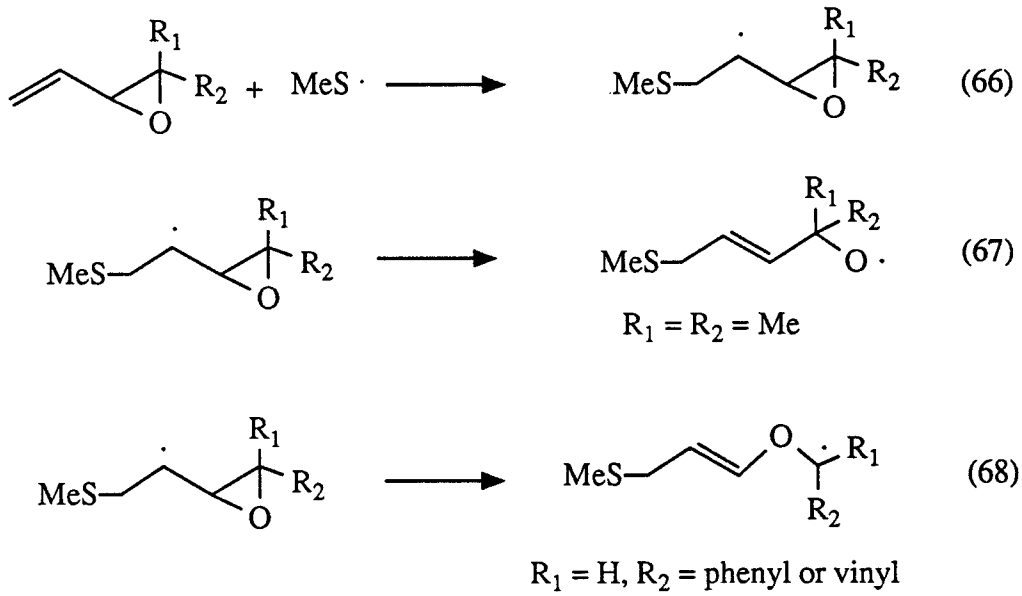
(64)

Attempts to observe this radical by ESR prior to rearrangement failed even at -116°.

Several other methods have been employed in order to generate β-epoxy radical. Three groups have reported studies involving the addition of radicals to butadiene monoepoxide.[76-78] Huyser and Munson generated cyclopentyl, cyclohexyl, and cyclooctyl radicals by treatment of corresponding cycloalkane with *t*-butyl peroxide, which then added to butadiene monoepoxide forming 1 : 1 adducts. A representative example is shown in equation 65.[76] Stogryn and Gianni have carried out



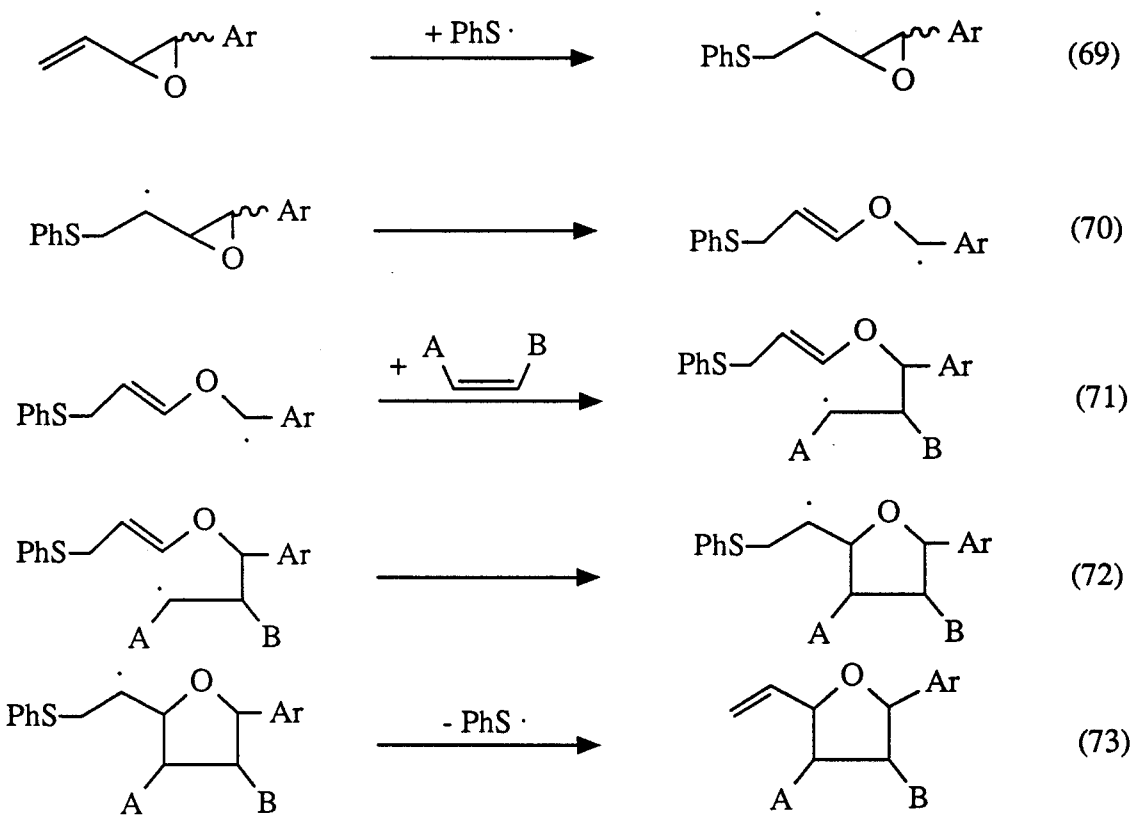
additions of methanethiol to substituted butadiene monoepoxides.[77] Their results demonstrate the effect of substitution on the course of ring opening (Scheme 16).



Scheme 16. Substituent effect on the course of β-epoxy radical rearrangement.

When the substituents at the epoxide carbon distal to the radical center are alkyl groups, ring opening occurs only *via* carbon-oxygen bond cleavage. However, when the substituent is phenyl or vinyl, ring opening occurs only *via* carbon-carbon bond

cleavage. The third reported instance of addition to a butadiene monoepoxide is due to Feldman and Fisher.[78] They found that thiyl radicals could initiate a two-step annulation sequence between an aryl substituted butadiene monoepoxide and an olefin (Scheme 17). The products are tetrahydrofurans in good yields.



Scheme 17. Annulation methodology using radical carbon-carbon bond cleavage of epoxides.

β-Bromo and β-chloroepoxides have also been used as precursors of β-epoxy radicals.[18,79-81] Reaction of these compounds with trialkyltin radicals leads to the formation of ring opened, allyloxyl radicals or vinylether radicals, depending on

substitution. Murphy *et al.* have recently used this method of radical generation to show an absence of stereoelectronic control in carbon-carbon bond cleavage for two diastereomeric chloroepoxides (Figure 8).[81]

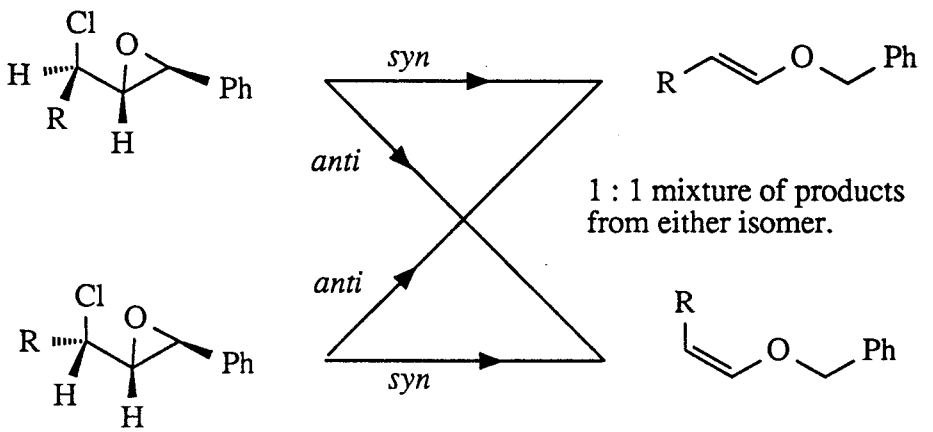
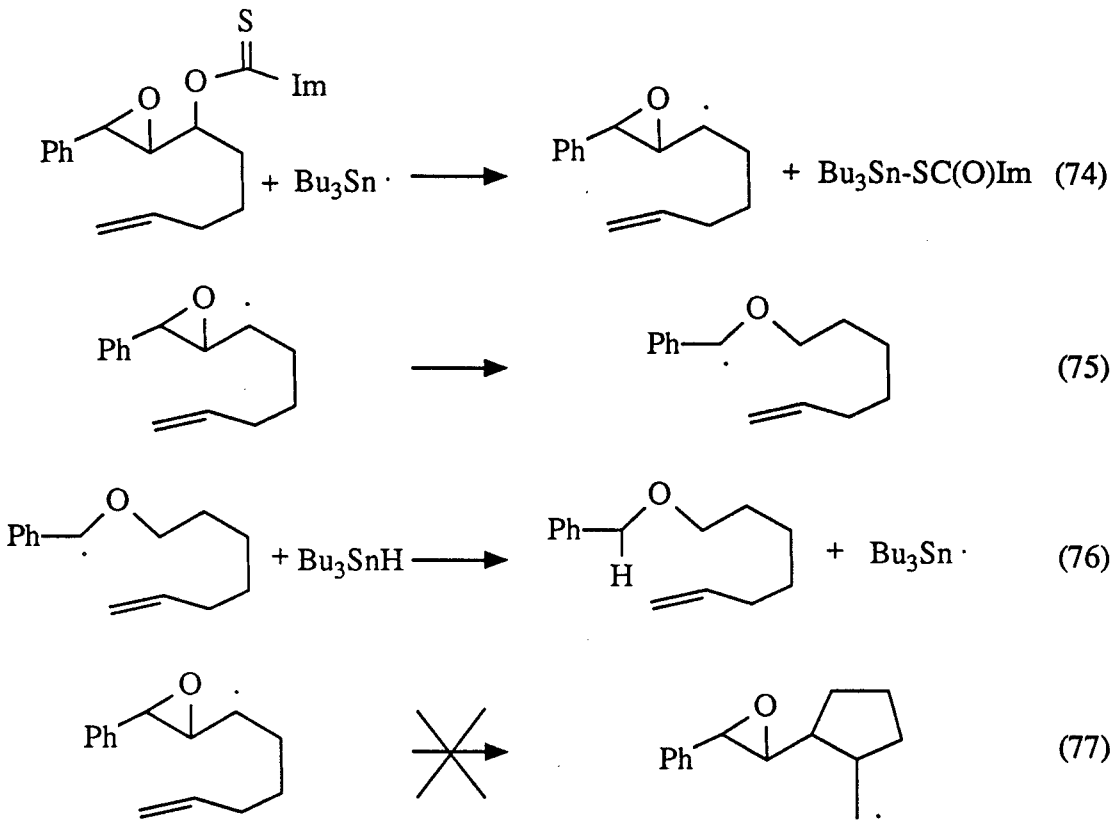


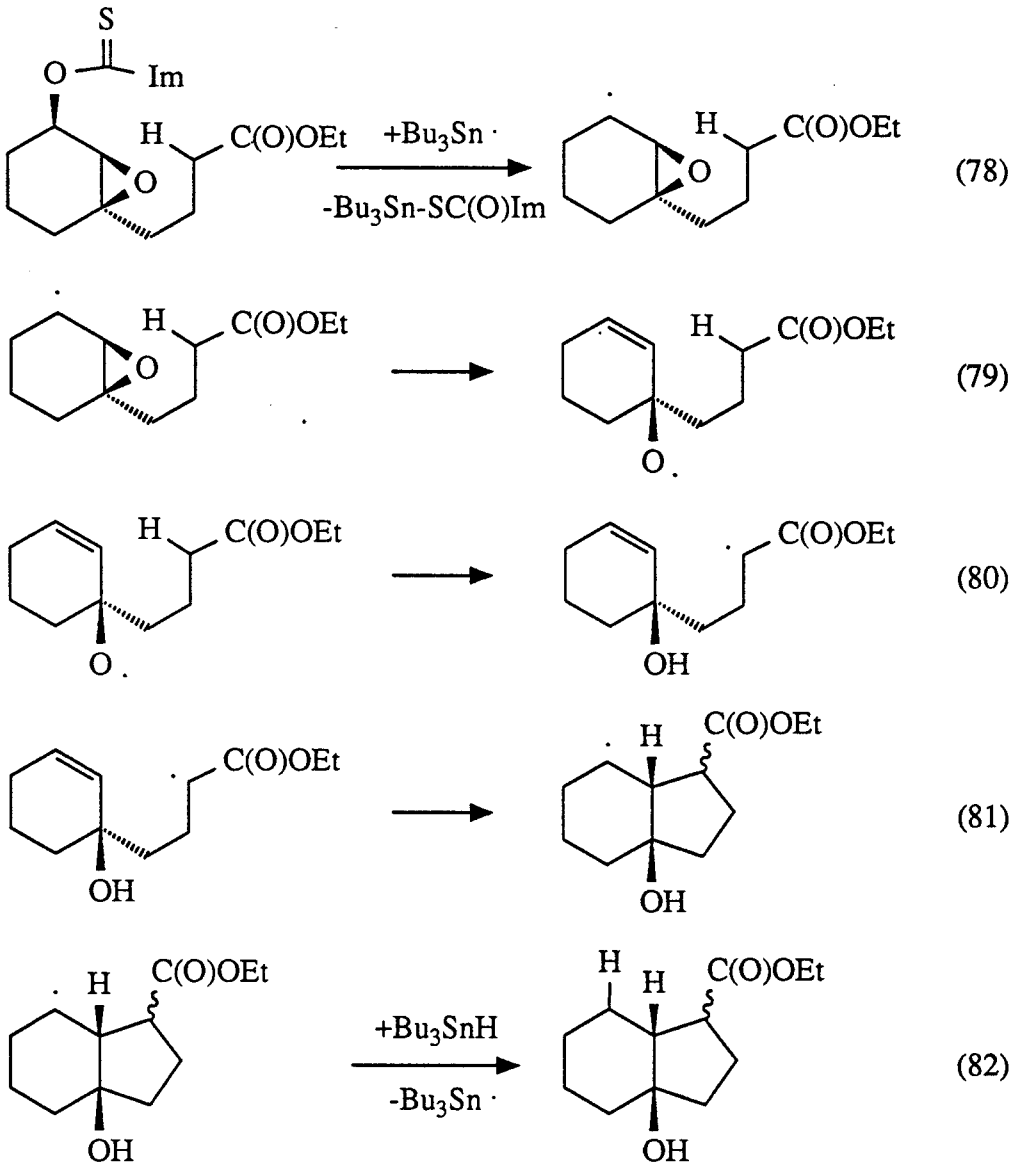
Figure 8. Stereochemical course of carbon-carbon bond breaking in the reduction of diastereomeric β-chloroepoxides with Bu_3SnH.[81]

In the same paper, thioimidazole esters were employed as β-epoxy radical precursors in an attempt to detect competition between carbon-carbon bond cleavage and cyclization of a 5-hexenyl radical (Scheme 18). It was found that the bond cleavage occurred exclusively.



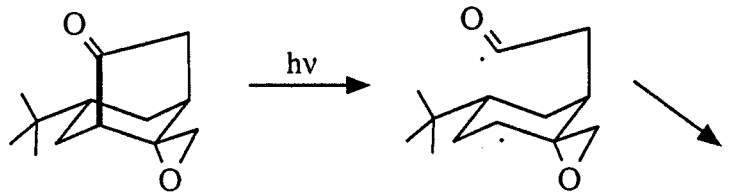
Scheme 18. Epoxide carbon-carbon bond cleavage in preference to 5-hexenyl radical ring closure.

A number of other groups have also used thioimidazole esters in order to study the rearrangement reactions of β-epoxy radicals.[82-84] An interesting application of this methodology has appeared recently.[84] Rawal and co-workers have constructed systems in which β-epoxy radicals, generated from thioimidazole precursors and tributyltin hydride, undergo a series of radical rearrangements, eventually forming fused ring compounds containing angular hydroxy groups (Scheme 19).

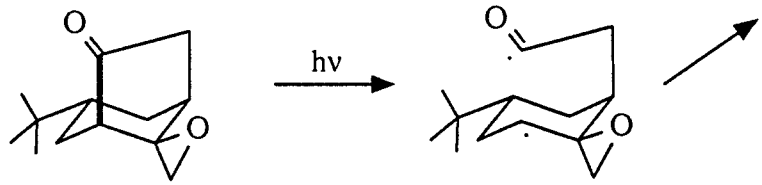


Scheme 19. Use of β-epoxy radical generation and rearrangement in the synthesis of carbocyclic rings.

Norrish Type I cleavages of photoexcited β,γ-epoxyketones generate biradicals in which one of the radical centers is β to the epoxide.[85-87] Agosta's group has demonstrated that photolysis of a pair of diastereomeric bicyclic β,γ-epoxyketones shows no stereoelectronic dependence of rates or products on the starting geometry (eqs. 83 and 84).[87] They have suggested, however, that zwitterionic contributing forms

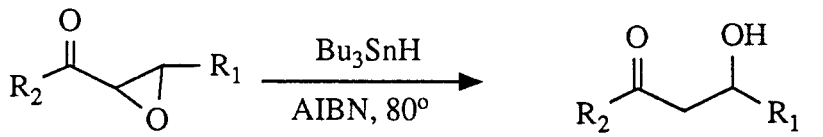


Same rates Same products (83)



(84)

of the biradical intermediates may complicate interpretation of the results in terms of radical fragmentation of epoxides. The reduction of α,β-epoxyketones with tributyltin hydride has been reported by Hasegawa *et al.*, to involve radical cleavage of epoxides (eq. 85).[88] In each case, β-hydroxyketones were the only reported products, even when



(85)

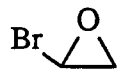
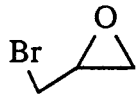
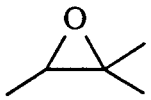
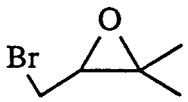
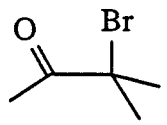
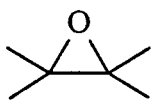
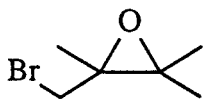
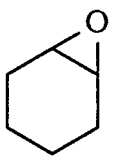
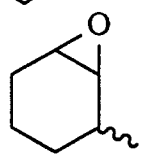
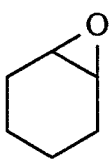
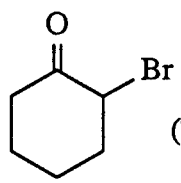
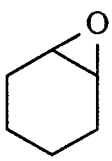
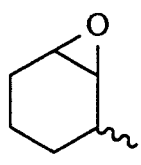
R_1 = H, phenyl, *p*-tolyl, i-propyl, n-pentyl
R_2 = phenyl or methyl

the substituent R was aromatic. The authors suggest that this anomalous result, carbon-oxygen bond cleavage as opposed to carbon-carbon bond cleavage, may be due to stereoelectronic effects caused by the oxygen-substituted radical interacting with the epoxide.

From the above discussion, several generalizations regarding the radical reactions of epoxides can be made. Hydrogen atom abstraction by electrophilic radicals occurs preferentially at the α positions of epoxides. In the one case where abstraction of a β hydrogen atom was reported, the temperature was very high (150°) and α hydrogen atom abstraction still accounted for a majority of the products.[71] Another point that is consistent in all of the above reports concerns the fate of β-epoxy radicals. In each case only ring opened products are observed. This is true for a large temperature range (-116° to 150°C).

One article has appeared which conflicts with the above generalizations.[89] The authors report the photoinitiated brominations of a number of epoxides with several brominating agents (Table 19). Based on the conditions employed, hydrogen atom abstraction occurs either exclusively at the α position or exclusively at the β position. When bromination at the β position is reported, no ring opened products are apparently observed. These results are difficult to justify based on the vast body of examples which have appeared, *vida supra*.

Table 19. Reported products for the bromination of several epoxides under various conditions.[a]

Starting epoxide.	Reaction conditions.	Reported products. (yield)
	NBS, hν, CCl_4, 15°	
	NBS, hν, CCl_4, 15°	
	NBS, hν, CCl_4, 15°	
	$BrCCl_3$, hν, CCl_4, 0°	 (65%)
	NBS, hν, CCl_4, 15°	
	NBS, hν, CCl_4, 15°	
	$BrCCl_3$, hν, CCl_4, 0°	 (70%)
	$BrNHCONH_2$, hν, CCl_4, 0°	 (56%)

a) Reference 89.

Based on the above review of the pertinent literature, it was decided that an investigation of the free radical chemistry of epoxides should be pursued. It was felt that any approach should address at least three vital issues:

1) The study should allow a direct comparison between the relative reactivities for radical generation at the differing regio- and stereoisomeric sites in an epoxide. With the exception of a rough estimate for the abstraction of hydrogen atoms from α and β positions in cyclohexene oxide, which can be extracted from the data of Sabatino and Gritter,[71] comparative reactivities for different positions have not been reported.

2) Experiments should be designed which would allow a determination of the inductive and resonance effects of the epoxide functional group in radical reactions.

3) An evaluation of possible stereoelectronic effects on radical generation in epoxides should be possible.

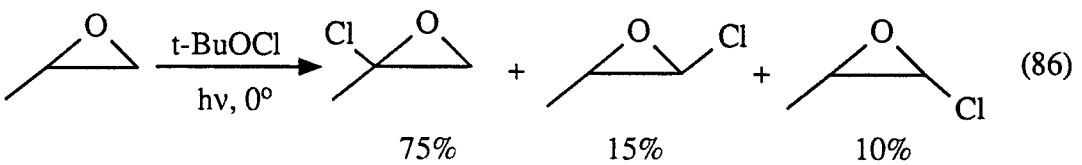
One system that promises to meet these criteria is halogen atom abstraction from a series of α- and β-chloroepoxides by triphenyltin radicals. Although this system differs greatly from hydrogen atom abstraction by electrophilic radicals, it offers an opportunity to conduct a position by position investigation of the ease of radical generation in epoxides. The triphenyltin radical is a nucleophilic species and is expected to show different reactivity preferences. Regio- and stereospecific chloroepoxides can be prepared and should allow for the measurement of relative rates of reaction.

Results and Discussion

Preparation of Compounds.

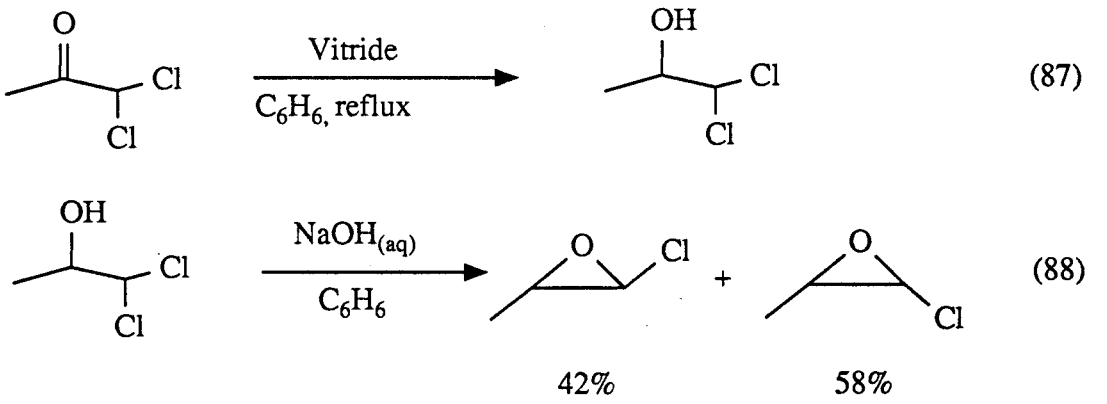
Of the compounds studied, only a few (epichlorohydrin, neophyl chloride, benzyl chloride, cyclohexyl chloride, and 1-chloro-2-methoxyethane) were available commercially. The others were prepared by the following methods.

Walling's photoinitiated chlorination of propylene oxide using *tert*-butyl hypochlorite[64] was repeated in order to prepare 2-chloro-1,2-epoxypropane. The reaction produced one major product (75%) and two minor products (15% and 10%) when carried out at 0°C. Isolation by preparative GC and characterization by NMR spectroscopy allowed identification of the products as 2-chloro-1,2-epoxypropane, *trans*-1-chloro-1,2-epoxypropane and *cis*-1-chloro-1,2-epoxypropane respectively (Eq. 86). No evidence for reaction at the exocyclic position of the propylene oxide was observed.

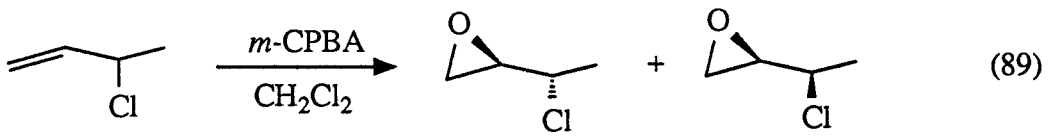


(86)

It proved more useful to prepare the *cis* and *trans*-1-chloro-1,2-epoxypropanes from 1,1-dichloroacetone by reduction to the alcohol using Vitride [Sodium dihydrobis(2-methoxyethoxy) aluminate], and base induced epoxidation (Eqs. 87 and 88). This method yielded a *trans*/*cis* ratio of 42/58.

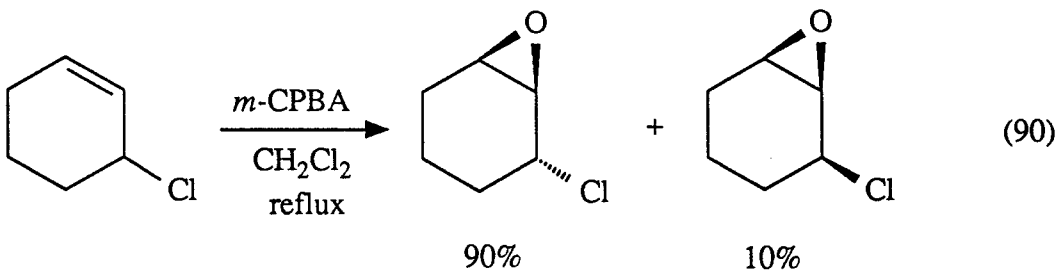


Erythro- and *threo*-2-chloro-3,4-epoxybutane were prepared from 3-chloro-1-butene by treatment with *meta*-chloroperbenzoic acid (*m*-CPBA)(eq. 89).[90]



This approach yielded a nearly one to one mixture of the two diastereomers which were separated by preparative GC. Identification of the diastereomers was based on comparison of the chemical shifts and coupling constants in the proton NMR spectra with published values.[91]

cis- and *trans*-2-chloro-7-oxabicyclo [4.1.0] heptane[92] were prepared in two steps from cyclohexene. Photoinitiated reaction of cyclohexene with *t*-butyl hypochlorite gave 3-chlorocyclohexene.[93] Epoxidation of 3-chlorocyclohexene with *m*-CPBA in dichloromethane gave a 90 : 10 mixture of diastereomers which were separated by preparative GC (eq. 90). Proton and carbon NMR spectroscopic data were



(90)

not sufficient to assign the stereochemistry of the two stereoisomers. Figure 9 shows the proton NMR of the major isomer and Figure 10 shows the proton NMR of the minor isomer.

In order to determine the stereochemistry of the major and minor isomers it proved necessary to open the epoxide rings using hydrochloric acid. Scheme 20 shows the results of treatment of each of the two isomers with concentrated hydrochloric acid.

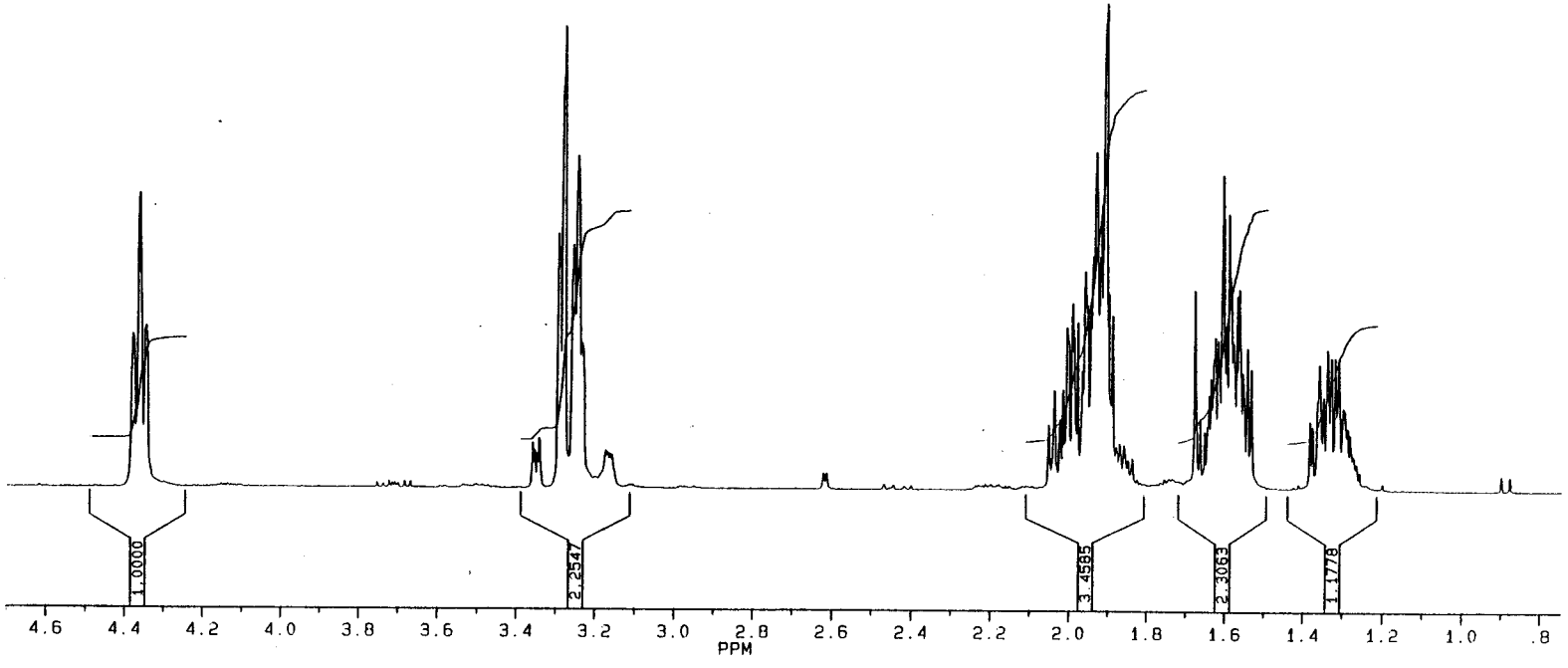


Figure 9. Proton NMR spectrum of the major isomer of 2-chloro-7-oxabicyclo[4.1.0]heptane.

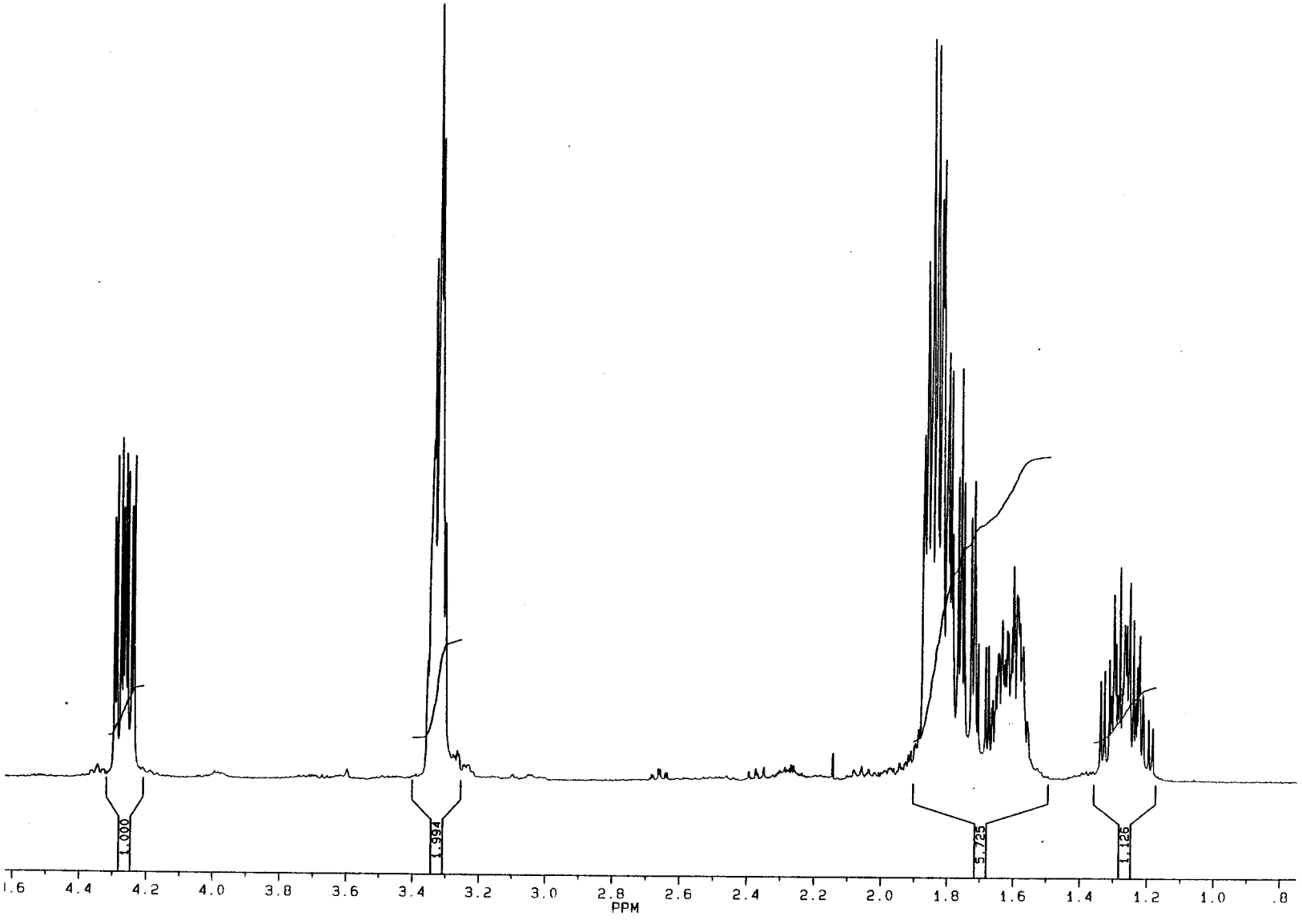
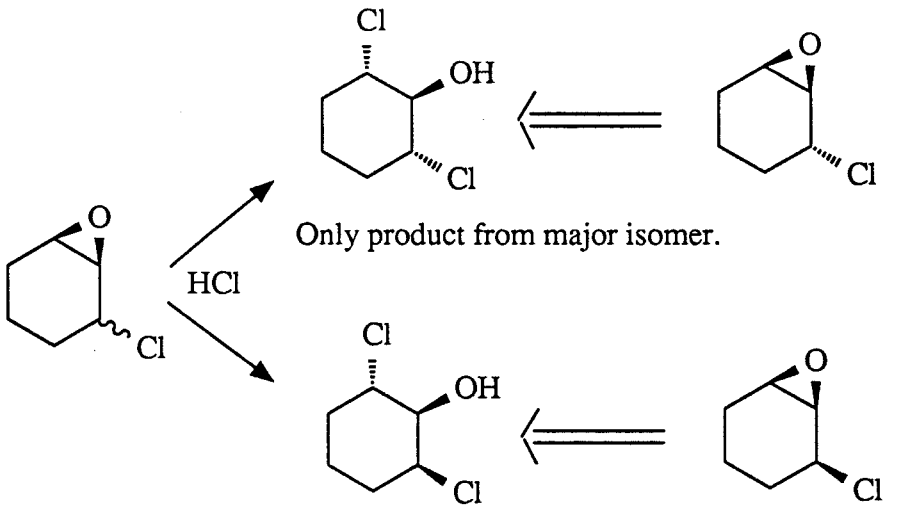


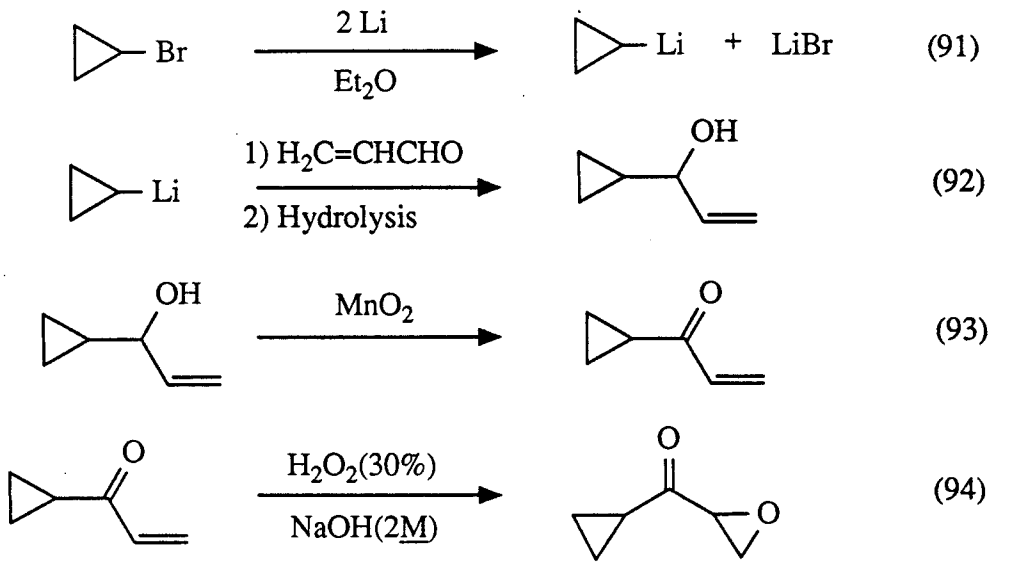
Figure 10. Proton NMR spectrum of the minor isomer of 2-chloro-7-oxabicyclo[4.1.0]heptane.



Scheme 20. Determination of stereochemistry for the two isomers of 2-chloro-7-oxabicyclo[4.1.0]heptane.

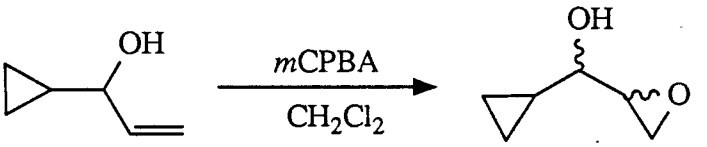
The product of the reaction of the major isomer with HCl was determined to be *trans, trans*-2,6-dichlorocycohexanol. The product of the reaction of the minor product with HCl was *cis, trans*-2,6-dichlorocyclohexanol. Assignment of the stereochemistry of each of the two diastereomers was made based on an expected mechanism of anti epoxide ring opening (Scheme 20).[94]

Cyclopropyloxiranylketone and the thiocarbonylimidazole ester of cyclopropyloxiranylmethanol have also been prepared. 1-Cyclopropyl-2-propen-1-ol, a common intermediate, was synthesized by preparation of cyclopropyl lithium[95] and reaction with acrolein (eqs. 91 and 92). Cyclopropyloxiranylketone was then prepared by oxidation with manganese dioxide[96] and epoxidation using hydrogen peroxide and sodium hydroxide[97] (eqs. 93 and 94).



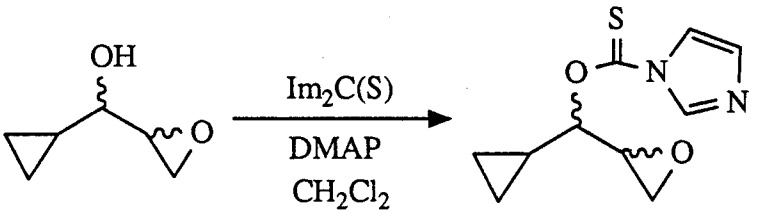
Scheme 21. Synthesis of cyclopropyloxiranylketone

Epoxidation of 1-cyclopropyl-2-propen-1-ol with *m*-CPBA afforded cyclopropyloxiranylmethanol as a 1 : 1 mixture of diastereomers (eq. 95). These diastereomers could not be separated. Treatment of the mixture of diastereomers with thiocarbonyldiimidazole, and catalytic N,N-dimethyl-4-aminopyridine (DMAP)[84] gave a similar diastereomeric mixture of the thiocarbonyl esters (eq. 96).



(95)

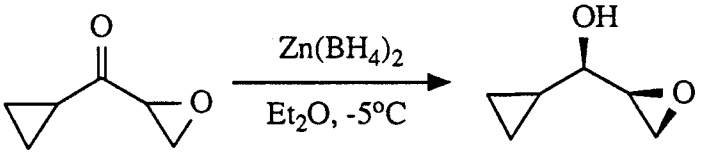
1 : 1 Mixture of diastereomers



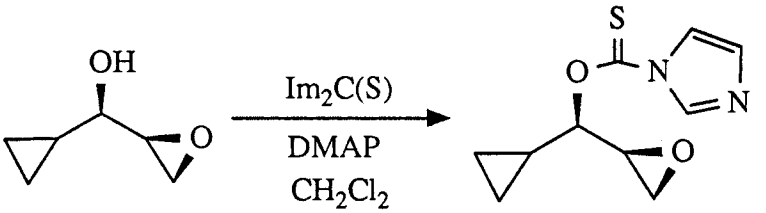
(96)

1 : 1 Mixture of diastereomers

Alternatively, the erythro isomer could be prepared selectively by reduction of cyclopropyloxiranylketone using zinc borohydride (eq. 97).[98] The erythro isomer of the thiocarbonyl ester was then prepared as above (eq. 98).



(97)

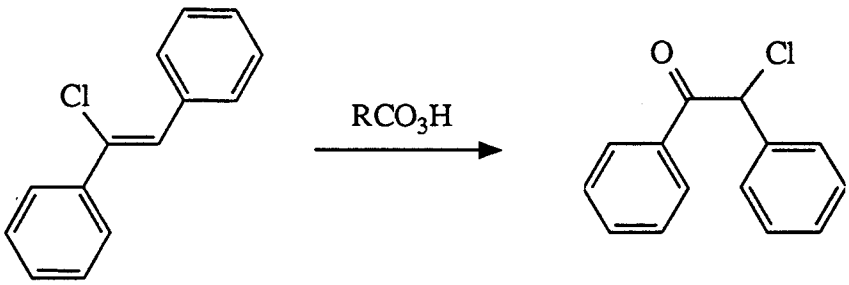


(98)

Kinetics.

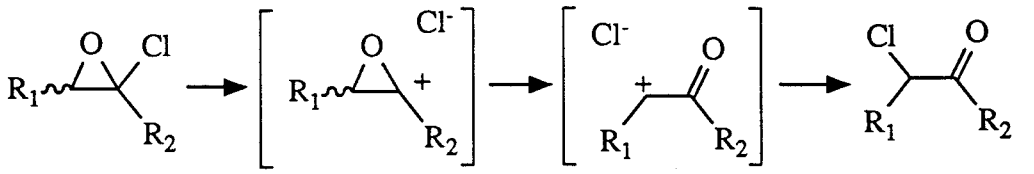
Relative rates of reaction for chloroepoxides were determined by running direct competitions between the compound being studied and a reference compound (either neophyl chloride or cyclohexyl chloride). Concentrations were determined relative to an internal standard using NMR integrations of characteristic signals or GC. Each of the reactions was run at 70°, in replicate.

α-Chloroepoxides have been reported to undergo rearrangement to α-chlorocarbonyl compounds under mild conditions.[99,100] McDonald and Schwab found that epoxidation of *trans*-α-chlorostilbene with peracids gave only 2-chloro-1,2-diphenylethanone (eq. 99).[99] They have proposed a rearrangement of the



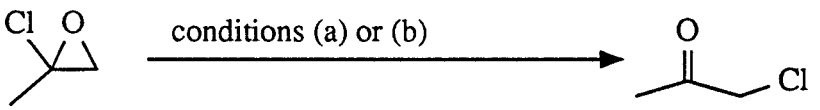
(99)

initially formed α-chloroepoxide. More recently, Gasteiger and Herzig have published their results on the preparation and thermal stability of nine different α-chloroepoxides.[100] Their findings suggest that the rearrangement is ionic in nature, proceeding by heterolysis of the carbon-chlorine bond (eq. 100).



(100)

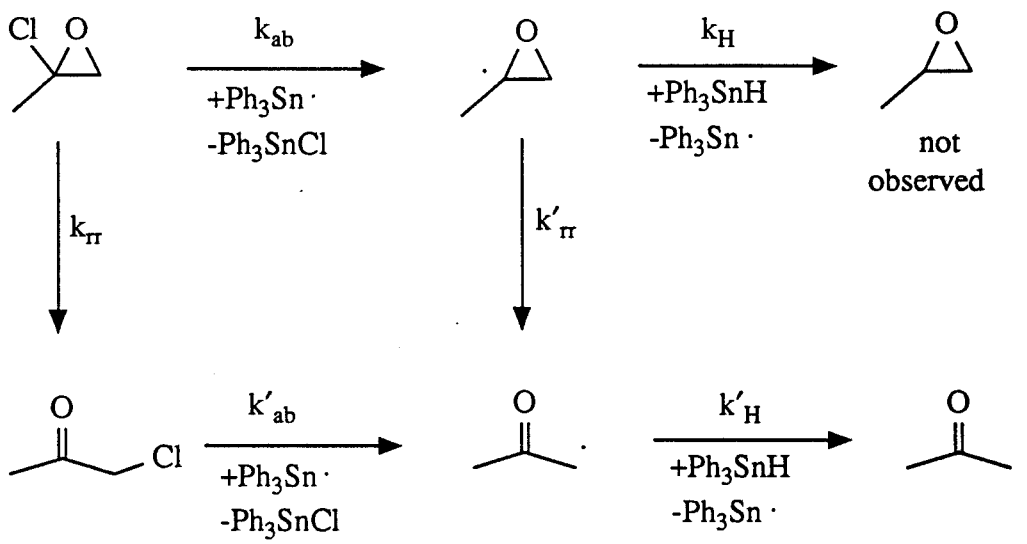
Similar rearrangement was observed for each of the α-chloroepoxides in this study. For example, 20-30% of a sample of 2-chloro-1,2-epoxypropane underwent isomerization to chloroacetone when stored in the refrigerator for two days. Addition of 1-2% hydrochloric acid to a sample of 2-chloro-1,2-epoxypropane has a dramatic accelerating effect on the rate of rearrangement, quantitative conversion to chloroacetone being observed within five minutes (eq. 101).



(101)

a) 0°C, 48hrs., 20-30%
b) 2% HCl, 5 min., 100%

The tendency of the α-chloroepoxides to rearrange complicated the study of these kinetics. Photoinitiated reaction of 2-chloro-1,2-epoxypropane with triphenyltin hydride in benzene-d_6 gave acetone as the sole product. There was no propylene oxide observed among the reaction products. Scheme 22 shows the possible routes to acetone. Similarly, the reaction of *cis*- and *trans*-1-chloro-1,2-epoxypropane under



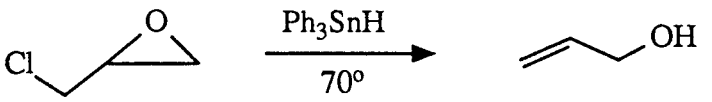
Scheme 22. Possible routes to acetone in the photoinitiated reaction of 2-chloro-1,2-epoxypropane with triphenyltin hydride.

identical conditions gave no indication that propylene oxide was formed. Although complicated by several new signals, NMR spectroscopy confirmed the presence of propionaldehyde as a major product.

The rates of disappearance for the α-chloroepoxides represent a sum of the rates of chlorine atom abstraction by the triphenyltin radical and rearrangement to α-chloroacetone or α-chloropropionaldehyde. These chlorocarbonyl compounds can then undergo reaction with triphenyltin hydride to yield ketone or aldehyde. Therefore, the relative rates of reaction for the α-chloroepoxides reported below should be considered as upper limits for the rates of chlorine atom abstraction from the starting chloroepoxides.

In contrast to the complicated picture which was observed for the α-chloroepoxides, epichlorohydrin, the simplest β-chloroepoxide, reacted to form only

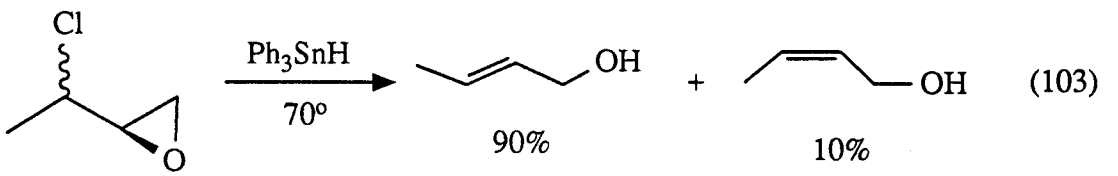
allyl alcohol (eq. 102). This is consistent with an early report by Kuivila for



(102)

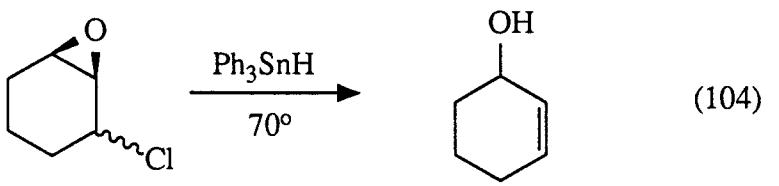
epibromohydrin.[18] The relative rate of chlorine atom abstraction from epichlorohydrin was twice that of cyclohexyl chloride.

Relative rates of reaction were also determined for the two pairs of diastereomeric β-chloroepoxides which were prepared. In the case of *erythro*- and *threo*-2-chloro-3,4-epoxybutane, reaction with triphenyltin hydride yielded the *trans*- and *cis*-2-buten-1-ols in a 90 : 10 ratio from either starting diastereomer (eq. 103).



(103)

Similarly, reaction of the *cis*- and *trans*-2-chloro-7-oxabicyclo[4.1.0]heptanes with triphenyltin hydride gave 2-cyclohexenol (eq. 104).



(104)

In order to compare the reactivities of the chloroepoxides with other systems, the relative rates of reaction for 1-chloro-2-methoxyethane and benzyl chloride were also determined under the reaction conditions employed. Table 20 contains a summary of the relative rates of reaction for each of the compounds studied.

Table 20. Relative rates for chlorine atom abstraction from chloroepoxides and other alkyl chlorides by triphenyltin radical at 70°.

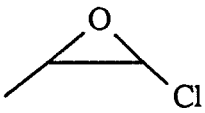
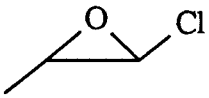
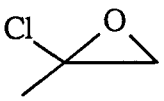
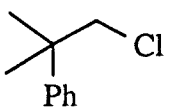
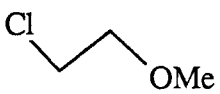
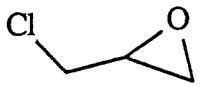
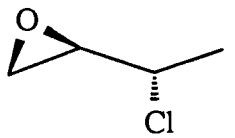
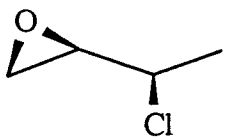
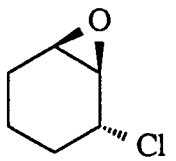
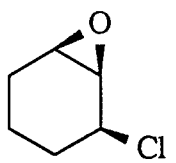
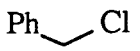
Substrate	Number of runs	k_{rel}
 *cis*-1-chloro-1,2-epoxypropane	3	0.031 ± 0.01
 *trans*-1-chloro-1,2-epoxypropane	3	0.036 ± 0.01
 2-chloro-1,2-epoxypropane	3	0.11 ± 0.01
 neophyl chloride	5	0.32 ± 0.03
 1-chloro-2-methoxyethane	6	0.40 ± 0.02
 cyclohexyl chloride	-	(1)

Table 20. Continued.

Substrate	Number of runs	k_{rel}
 epichlorohydrin	3	2.00 ± 0.02
 *erythro*-3-chloro-1,2-epoxybutane	4	5.19 ± 0.14
 *threo*-3-chloro-1,2-epoxybutane	4	5.78 ± 0.20
 *trans*-2-chloro-7-oxabicyclo[4.1.0]heptane	5	5.46 ± 0.28
 *cis*-2-chloro-7-oxabicyclo[4.1.0]heptane	3	11.1 ± 1.0
 benzyl chloride	3	22.5 ± 1.5

Discussion.

The relative reactivities of the four isomers of chloropropylene oxide with triphenyltin hydride follow a trend which would be expected based on a model involving negative charge development on the chlorine bearing carbon in the transition state. This model is generally accepted for chlorine abstraction reactions by trialkyltin radicals (see introduction, pp 7-9). The chlorine atom abstraction from α-chloroepoxides should be disfavored because it involves the development of negative charge on an atom which is adjacent to an oxygen atom (Figure 11).

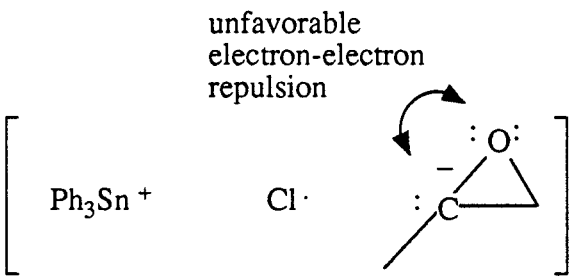


Figure 11. Effect of negative charge development in the transition state of chlorine atom abstraction from 2-chloro-1,2-epoxypropane.

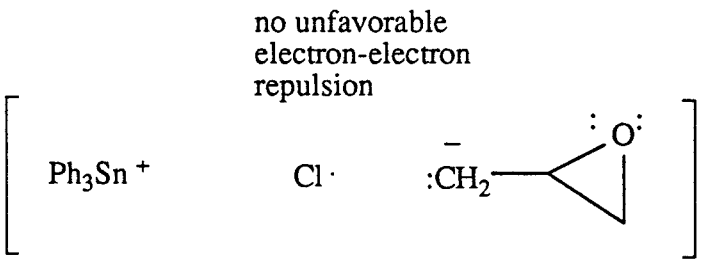


Figure 12. Effect of negative charge development in the transition state of chlorine atom abstraction from epichlorohydrin.

Conversely, chlorine atom abstraction from β-chloroepoxides should be favored due to the stabilizing effect of the oxiranyl substituent (Figure 12). Dannen and co-workers have measured the effect of the *p*-oxiranyl substituent on the delocalization of several aromatic radical anions.[101] From their results, it was possible to determine a sigma value of +0.14 for *p*-oxiranyl. This positive value indicates the oxirane's ability to stabilize neighboring negative charge. In contrast, the same study reports a sigma value of -0.10 for *p*-cyclopropyl, suggesting an electron donating ability.

This description of the transition state is also supported by attempted correlations of the logarithms of the relative rates of reaction with calculated energy differences between each starting chloroepoxypropane and an intermediate cation, radical, radical anion, or anion. These semiempirical calculations were carried out at the AM1 level.[102] Table 21 contains a summary of the results of these attempted correlations. The optimum correlation of reactivity with calculated energy differences requires both a negative slope, indicating that as the energy difference decreases the rate of reaction increases, and a high correlation coefficient. These are observed only for the case where the intermediate anions are used. This again demonstrates that the ability of a substituent to stabilize negative charge development is related to the relative reactivity in chlorine atom abstraction reactions.

Table 21. Results of attempted correlations of the logarithms of the relative rates of reaction of the isomeric chloroepoxypropanes with calculated energy differences between starting chloroepoxide and an intermediate.[a]

Intermediate	Sign of slope	Correlation coefficient (r)
Anions	negative	0.99
Radicals	negative	0.75
Cations	positive	0.98
Radical Anions (Adiabatic)[b]	negative	0.71
Radical Anions (Isothermal)[c]	positive	0.78

a) Calculations were carried out by the AM1 approach.
b) Geometry of the radical anions was minimized.
c) Geometry of the radical anions was held the same as for the starting chloroepoxides.

The rate accelerating ability of the oxiranyl substituent is due to its ability to stabilize negative charge development in the transition state of chlorine atom abstraction. However, to what degree is this stabilization due to the inductive effect of the electronegative oxygen atom (Figure 13) or to the conjugative effect of the three membered ring (Figure 14)?

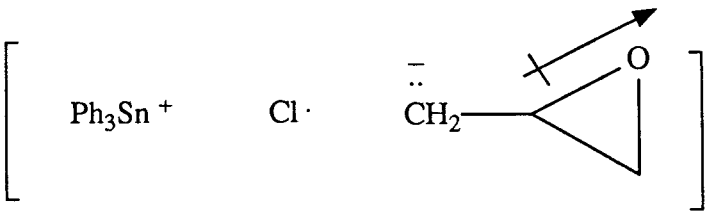


Figure 13. Depiction of inductive stabilization of developing negative charge in the transition state by the oxiranyl substituent.

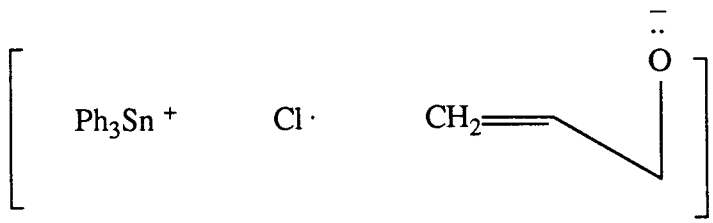
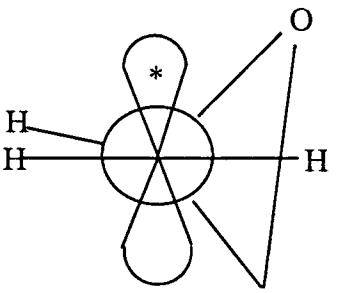


Figure 14. Additional canonical form for the transition state of chlorine atom abstraction, depicting conjugative stabilization of developing negative charge.

The importance of the inductive effect can be examined by considering the relative reactivities for epichlorohydrin and an acyclic β-chloroether.[105] From Table 20 it can be seen that epichlorohydrin is 5.0 times more reactive than the structurally similar 1-chloro-2-methoxyethane. The oxygen atoms in these compounds should exert nearly equivalent inductive effects on the reaction sites. While the β-chloroether is slightly more reactive than neophyl chloride (a primary alkyl chloride), it is apparent

that inductive stabilization of negative charge development cannot completely account for the increased reactivity observed for the β-chloroepoxides.

Dannen has carried out semi-empirical molecular orbital calculations of oxiranylcarbinyl cations, radicals, and anions.[106] He predicted, based on those calculations, that the greatest conjugative stabilization should be achieved with a bisected geometry (Figure 15). The effect of geometry on the extent of conjugation should be observable as a stereoelectronic attenuation of the rate of reaction for β-chloroepoxides which differ only in their geometries (i.e. diastereomers).



* The orbital may contain two, one, or no electrons.

Figure 15. Bisected geometry for oxiranylcarbinyl anion, radical, and cation.

Erythro- and *threo*-2-chloro-3,4-epoxybutane reacted at nearly the same rate with triphenyltin hydride (Table 20). Both compounds were more than five times as reactive as cyclohexyl chloride; however, no definitive stereoelectronic effect on the rates was observed. This may be due in part to the conformational flexibility of the monocyclic β-chloroepoxides.

In contrast to the similar rates observed for the chloroepoxybutanes, the two diastereomeric bicyclic β-chloroepoxides reacted at quite different rates. The cis compound had a relative rate slightly more than twice that observed for its trans isomer. In order to assess the origin of this rate effect, geometry minimizations at the

AM1 level have been carried out on each of the isomers.[102] Two conformations corresponding to energy minima were found for each isomer. The oxygen-carbon-carbon-chlorine dihedral angles (<OCCCl) and energies (ΔH_f) for each conformation are shown in Figure 16.

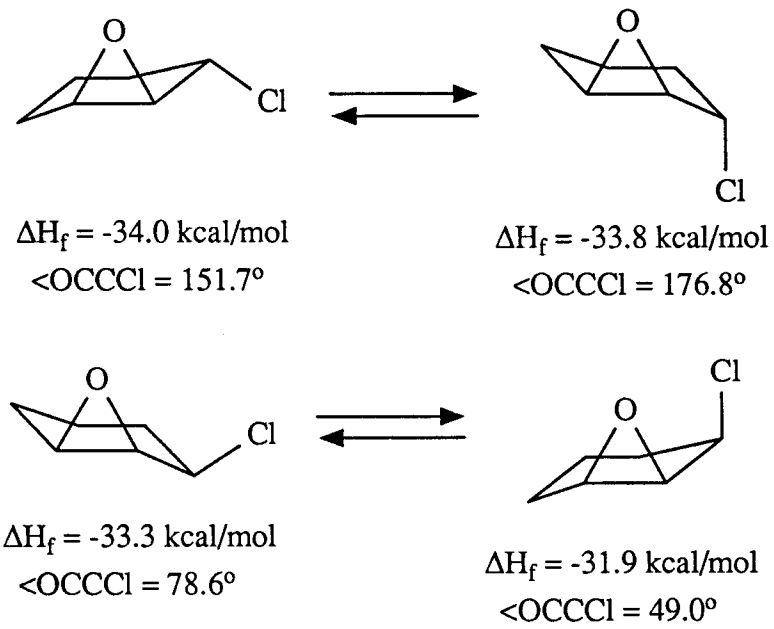


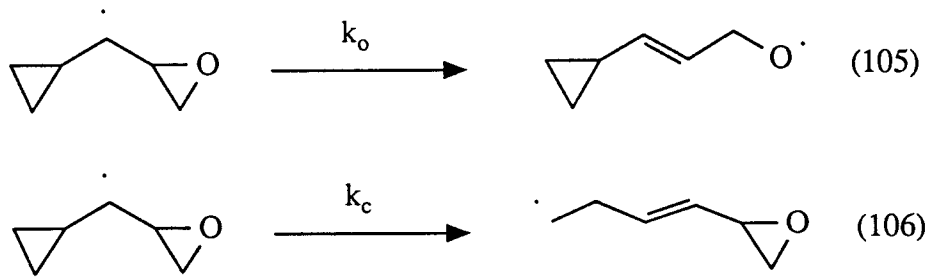
Figure 16. Summary of AM1 calculations for *trans*- and *cis*-2-chloro-7-oxabicyclo[4.1.0]heptanes.

It is difficult to predict which conformation should facilitate conjugative stabilization of negative charge development to the greater degree. However, the energy differences between the isomers are of the right magnitude to suggest another explanation for the observed rates. The cis compound has a higher energy by 0.7 kcal/mol. Relief of this excess strain energy in the transition state could act as a driving force for reaction of the more highly strained isomer. An energy difference of 0.7 kcal/mol corresponds to a relative rate of about 2 to 1. Therefore, it may be

difficult to assign any part of the rate difference to a stereoelectronic effect.

Another interesting aspect of β-epoxy radicals is their strong tendency toward ring opening rearrangement. In fact no reports of chemical trapping or spectroscopic observation of a β-epoxy radical prior to rearrangement have appeared. Murphy's group have attempted to trap a phenyl substituted β-epoxy radical prior to carbon-carbon bond cleavage by incorporating into their system a potentially competing intramolecular 5-hexenyl ring closure (see Scheme 18).[81] They found that no five membered ring products were formed, indicating that the epoxide fragmentation was at least two orders of magnitude faster than closure to form a cyclopentylmethyl radical.

Intramolecular trapping remains a good idea. It is possible that a more effective trap and a slower epoxide rearrangement might lead to a system which would be amenable to trapping the β-epoxy radical. Attention was turned toward systems by which the oxiranylcyclopropylcarbinyl radical could be generated in the presence of a hydrogen atom source. The formation of this radical should allow comparison of oxiranyl ring opening with cyclopropyl ring opening (Eqs. 105 and 106). The ratio of

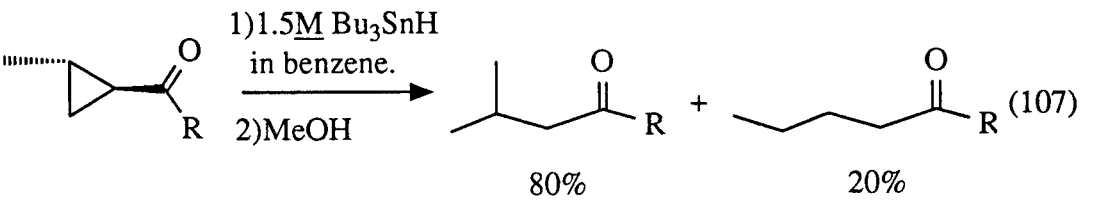


concentrations of ring opened products would be equal to the ratio of the rate constants for ring opening in either direction (k_o/k_c), provided kinetic control governed both processes. Furthermore, the kinetics of cyclopropylcarbinyl radical ring opening have

been extensively studied.[72] Therefore, a comparison of relative rates of ring opening for oxiranyl and cyclopropyl rings will also allow estimation of the rate constant for the oxiranylcarbinyl radical rearrangement.

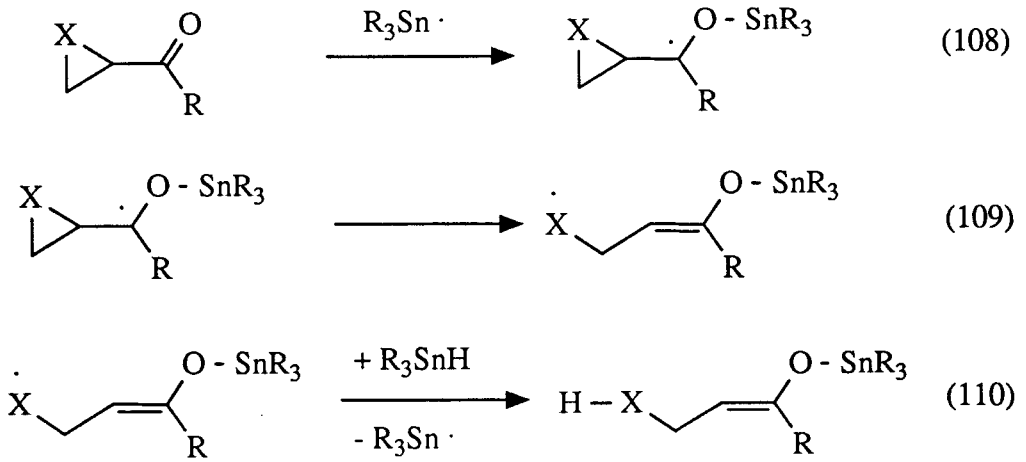
One obvious possible method for generation of this radical was by reaction of the corresponding β-chloroepoxide. Synthetic attempts to prepare this compound were unsuccessful.

α,β-Epoxyketones have been reported to be sources of β-epoxy radicals in reaction with trialkyltin hydrides.[88] Similarly, cyclopropylcarbinyl radicals have been generated from cyclopropylketones, again using trialkyltin radicals.[107-109] In the case of substituted cyclopropylketones, Davies *et al.* have shown that a tri-*n*-butyltin hydride concentration of 1.5 M is necessary in order to establish kinetic control of the regiochemistry of ring opening (eq. 107).[107] Similar mechanisms, involving trialkyltin



(107)

radical attack at the carbonyl, have been suggested for reactions of cyclopropylketones and oxiranylketones with trialkyltin hydride (Scheme 23).



Scheme 23. Proposed mechanism for reaction of trialkyltin hydride with cyclopropylketones ($X=CH_2$),[107] and oxiranyl-ketones ($X=O$).[88]

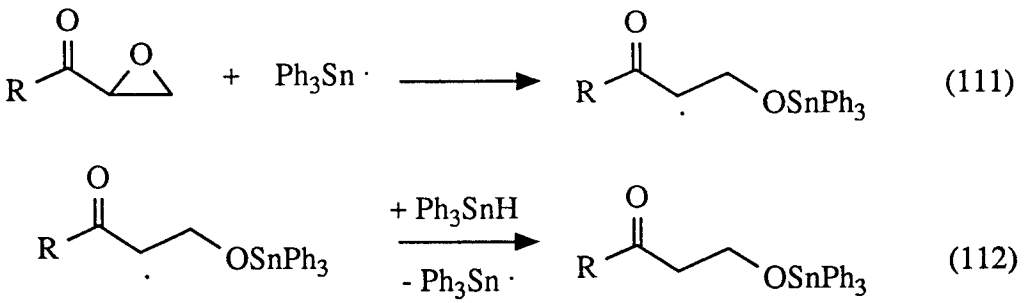
It was hoped that treatment of cyclopropyloxiranylketone with triphenyltin hydride would generate a radical which would then partition between cyclopropyl ring opening and epoxide ring opening. Methylcyclopropylketone and methyloxiranylketone were also studied as model compounds. In each case, the substrate was added to a 2.0 M solution of triphenyltin hydride in benzene-d_6 with 3-5% AIBN. The reaction mixtures were sealed in pyrex ampules and immersed in an oil bath at 70° for one hour. The reactions were then evaluated by ^{1}H-NMR spectroscopy. Table 22 contains the results of these experiments.

Table 22. Results of reaction of triphenyltin hydride with oxygen containing substrates at 70°C.[a]

Starting compound	Observed product	Percent conversion
cyclopropylmethylketone	no reaction	--
oxiranylmethylketone	4-hydroxy-2-butanone	100%
cyclopropyloxirany-ketone	3-hydroxy-1-cyclopropyl-1-propanone	90-100%
styrene oxide	2-phenylethanol	60%

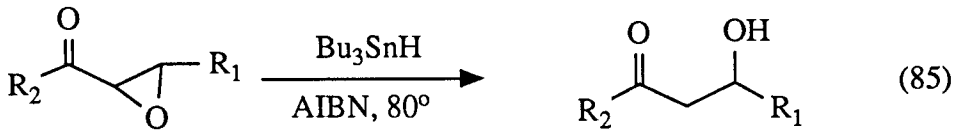
a) Conditions: 2.0 M Ph_3SnH, benzene-d_6, 3-5% AIBN, 70°C, 1.0 hrs.

The dramatic differences in reactivity between cyclopropyl- and oxiranylketones suggest that an alternate mechanism might be operative. In order to examine this possibility further, styrene oxide was also reacted with triphenyltin hydride under identical reaction conditions (Table 22). The observed reactivity of styrene oxide and the formation of the ring opened product, suggest that the triphenyltin radical may be directly reacting with the epoxide oxygen. This may also be the case for the α,β-epoxyketones. A possible mechanism involving attack by the triphenyltin radical at the epoxide oxygen is shown in Scheme 24.



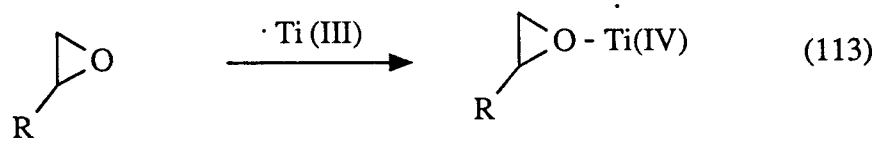
Scheme 24. Possible S_H2 mechanism for reaction of triphenytin hydride with α,β-epoxyketones.

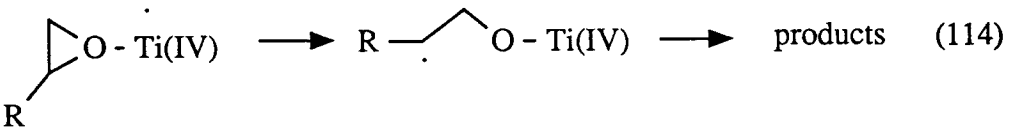
This mechanism also accounts for the apparently anomalous results which were reported for aryl substituted α,β-epoxyketones (eq. 85).[88]



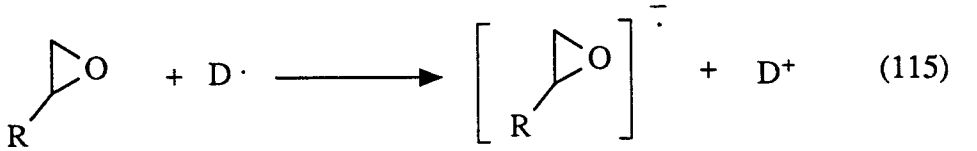
R_1 = H, phenyl, *p*-tolyl, i-propyl, n-pentyl
R_2 = phenyl or methyl

A direct attack on the ether oxygen has never been proposed for the reaction of triphenyltin radicals with epoxides. A similar mechanism, however, has been suggested for the reaction of epoxides with paramagnetic titanium(III) complexes (eqs. 113 and 114).[110-112]





It is also possible that the reaction is proceeding through single electron transfer from the triphenyltin radical to the epoxide to form an epoxy radical anion. Precedent for this type of reaction may be found in the reactions of Freeman's reagent (lithium 4,4′-di-*tert*-butylbiphenylide),[113] and other electron donors with epoxides,[114-116] epoxyketones,[117] and phenyl substituted epoxides (eq. 115).[118]

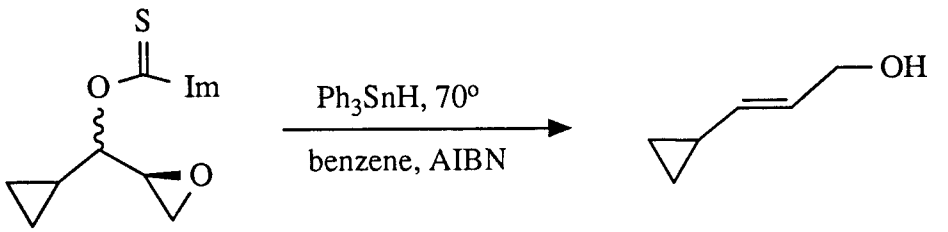


D · = electron donor

It is important to point out that these are preliminary findings. Although further work on the mechanism of this reaction should prove fruitful, it does not address the rate of ring opening for a β-epoxy radical. In order to determine a value for the ring opening rate of β-epoxy radicals, another method of radical generation was sought.

Based on the reports of several groups who have used thiocarbonylimidazole

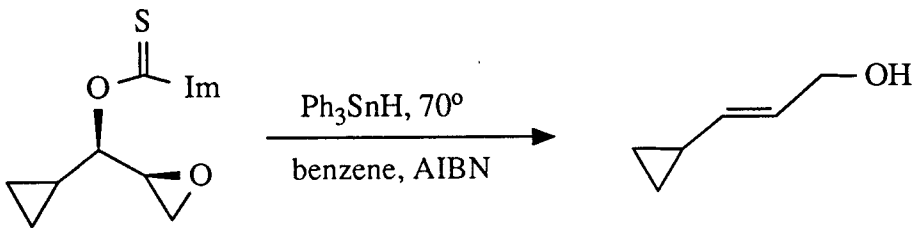
esters to generate β-epoxy radicals,[81-84] it was felt that this type of precursor might serve to generate the cyclopropyloxiranylmethyl radical. Treatment of a 1:1 mixture of diastereomers of the thiocarbonylimidazolide of cyclopropyloxiranylcarbinol in benzene-d_6 with 1.1 equivalents of triphenyltin hydride and 5% AIBN gave predominantly the product of epoxide ring opening (eq. 116). The NMR spectrum of



(116)

the product mixture was complicated by signals from a number of minor products. In an effort to simplify the analysis of the reaction, the erythro isomer of the thioimidazole precursor was prepared.

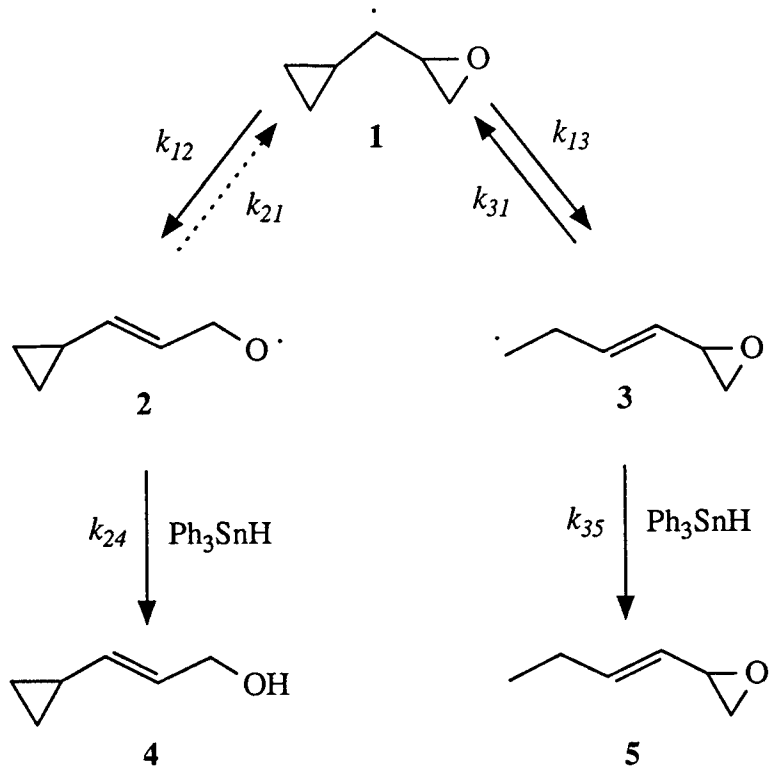
Treatment of the erythro diastereomer with 7-19 equivalents of triphenyltin hydride (1-2.3 M) at 70° gave *trans*-3-cyclopropyl-2-propen-1-ol as the only observable product by ^{1}HNMR spectroscopy (eq. 117).



(117)

The overall scheme for formation of the two possible products is shown in Scheme 25. Each structure in Scheme 25 has been assigned a number in order to

facilitate a discussion of the kinetics. The rate constants are labeled by the reaction they represent, for example, k_{12} is the rate constant for the reaction of **1** going to **2**.



Scheme 25. Overall kinetic scheme for formation of **4** and **5** from radical **1**.

The ratio of products **4/5** is represented by equation 118. This equation is obtained by assuming steady state concentrations for radicals **2** and **3**. Defining the

$$\frac{4}{5} = \frac{k_{12}}{k_{13}} \times \frac{k_{24}\,(k_{31} + k_{35}\,[Ph_3SnH])}{k_{35}\,(k_{21} + k_{24}\,[Ph_3SnH])} \qquad (118)$$

quantity **Q** as shown in equation 119 yields the expression for the ratio of products that

is shown in equation 120. From equation 120 it can be seen that the ratio of products

$$\mathbf{Q} = \frac{k_{24}\,(k_{31} + k_{35}\,[Ph_3SnH])}{k_{35}\,(k_{21} + k_{24}\,[Ph_3SnH])} \qquad (119)$$

$$\frac{\mathbf{4}}{\mathbf{5}} = \frac{k_{12}}{k_{13}} \times \mathbf{Q} \qquad (120)$$

will represent the ratio of ring opening rate constants only when **Q** is equal to 1. This requirement translates into a question of the importance of the reversibility of each of the two ring opening steps.

No report of allyloxyl radicals such as **2** cyclizing to **1** has appeared. However, its importance can be assessed by considering the effect that reversibility of oxiranyl ring opening would have on the ratio of **4/5** and the ratio of k_{12}/k_{13}. If the rearrangement of **2** to **1** is occurring, it will increase the amount of product **5** which is formed and yield a value of k_{12}/k_{13} that is too low. Since only a lower limit of the ratio of rate constants can be obtained (because no formation of **5** was observed), the reaction of **2** going to **1** can be dismissed. Therefore, for the purpose of determining a lower limit for the ratio k_{12}/k_{13} it can be assumed that $k_{21} << k_{24}[Ph_3SnH]$. This assumption yields a simplified expression for **Q** (eq. 121). From this expression, it can

$$\mathbf{Q} = \frac{k_{31} + k_{35}\,[Ph_3SnH]}{k_{35}\,[Ph_3SnH]} = \frac{k_{31}}{k_{35}\,[Ph_3SnH]} + 1 \qquad (121)$$

be seen that the relationship between the ratio of the products formed and the ratio of the rate constants is governed by the relative rates of cyclization of **3** to **1** and trapping of **3** by triphenyltin hydride. Three possible relationships between these two rates

should be considered. Firstly, **Q** will be equal to 1 if trapping of radical **3** by triphenyltin hydride is much faster than ring closure of **3** to **1**, i.e. $k_{35}[Ph_3SnH] >> k_{31}$. Secondly, if the rates of cyclization and trapping are similar, then **Q** will have a value greater than 1. For example, if the rates were equal, then the ratio of products would actually represent twice the ratio of ring opening rate constants. Thirdly, if cyclization was much faster than trapping, then the ratio $k_{31}/k_{35}[Ph_3SnH]$ would become very large and the product ratio would not represent the ratio of ring opening rates at all.

The rate of hydrogen atom transfer from triphenyltin hydride to various radicals has been studied (Table 23). Carlsson and Ingold found that the rate for hydrogen atom transfer from tin hydrides to *tert*-butyl radicals was somewhat dependent on the nature of the tin substituents.[119] Similar results have been reported by Ingold *et al.* for

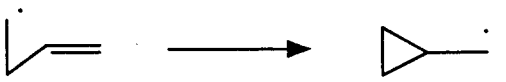
Table 23. Absolute rate constants for reactions of some radicals with trialkyltin and triaryltin hydrides.

Reaction	k_H, at $\approx 25°C(\underline{M}^{-1}\ sec^{-1})$
t-butyl· + Ph_3Sn-H [a]	3.1×10^6
t-butyl· + *n*-Bu_3Sn-H [a]	7.4×10^5
t-butyl· + Me_3Sn-H [a]	2.9×10^5
t-butoxyl· + Ph_3Sn-H [b]	1.9×10^8
t-butoxyl· + *n*-Bu_3Sn-H [b]	4.3×10^8
RCH_2CH_2· + *n*-Bu_3Sn-H [c]	2.7×10^6

a) Reference 119.
b) Reference 120.
c) Reference 121.

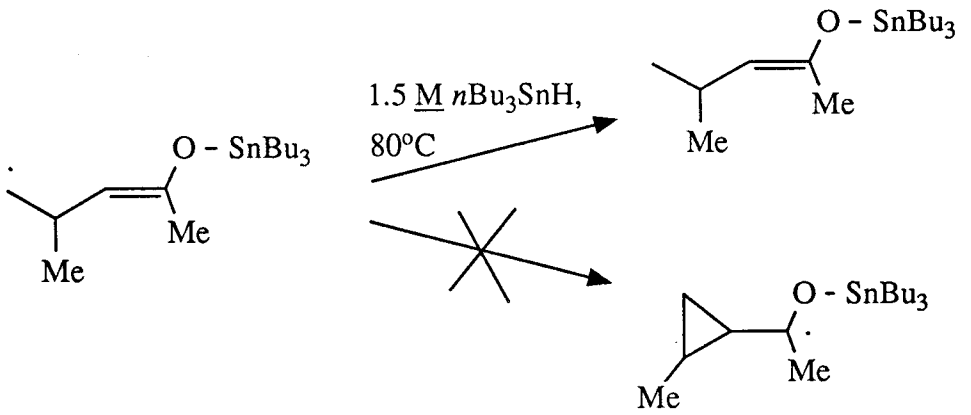
hydrogen abstraction from tin hydrides by the more reactive *tert*-butoxyl radical.[120] In this case, the rate of hydrogen transfer from triphenyltin hydride is twice as fast as it is for tri-*n*-butyltin hydride. Hydrogen atom transfer from tri-*n*-butyltin hydride to a primary radical has been measured over the temperature range of -30 to 80°C.[121] The rate constant is 3.0 X 10^6 $\underline{M}^{-1}sec^{-1}$ at 80°. Based on the relationship between triphenyltin hydride and tri-*n*-butyltin hydride (a factor of at least 2), and the use of a 2.3 $\underline{M}$ solution of triphenyltin hydride, a reasonable estimate for $k_{35}[Ph_3SnH]$ is 1.4 X 10^7 sec^{-1}.

It is more difficult to arrive at estimates for the value of k_{31}. For the cyclization of unsubstituted 3-butenyl radicals (eq. 122), a rate constant of 8.0 X 10^3 sec^{-1} has been reported for reaction at 25°.[122,123] This is certainly much smaller than the rate for



(122)

trapping with triphenyltin hydride, however, the cyclization of **3** to **1** forms a more stable secondary radical which should increase the rate of ring closure. For this reason, empirical evidence must be relied upon. Davies *et al.* found that at 80°, a tri-*n*-butyltin hydride concentration of 1.5 $\underline{M}$ was sufficient to trap their substituted 3-butenyl radical prior to ring closure (eq. 123).[107] This radical should cyclize faster than radical **3**



(123)

because it forms an oxygen stabilized radical and because methyl substitution at the 2 position has been shown to accelerate ring closure of 3-butenyl radicals.[123] It is reasonable to expect that the use of a larger concentration of a better hydrogen atom donor should be sufficient to trap a slower radical rearrangement (**3** to **1**).

Since the ratio **4/5** is >100, the rate constant for oxiranylcarbinyl radical ring opening is at least two orders of magnitude faster than the rate constant for ring opening of cyclopropylcarbinyl radical. Furthermore, Ingold *et al.* have used a statistical correction in cyclopropylcarbinyl ring opening to account for the two identical bonds which can be cleaved.[122] Therefore, the relationship between the rate constants for ring opening is: $k_{12} > 200 \times k_{13}$. If a rate constant of 2.6×10^8 sec^{-1} for cyclopropylcarbinyl radical ring opening is used,[124] then the rate constant for oxiranylcarbinyl radical ring opening is greater than 5×10^{10} sec^{-1}! This first order rate is faster than diffusion control of bimolecular processes[125] and suggests that the unrearranged oxiranylcarbinyl radical will forever elude bimolecular trapping, no matter how effective the trap.

Conclusions.

The rates of chlorine atom abstraction from isomeric chloroepoxides follow the expected trend based on a model involving negative charge development in the transition state. α-Chloroepoxides react at a much slower rate than do β-chloroepoxides with triphenyltin radicals. The β-chloroepoxides are more reactive than alkyl chlorides, apparently due to both inductive and conjugative effects of the epoxide. Relative rate differences for two pair of diastereomeric β-chloroepoxides were not assignable to a specific stereoelectronic effect of the epoxide. Intramolecular competition between cyclopropylcarbinyl and oxiranylcarbinyl radical rearrangements set a lower limit on the rate of ring opening for β-epoxy radicals which is faster than diffusion control.

Experimental

Procedures

Gas chromatographic analysis was carried out with a Varian 3400 capillary gas chromatograph equipped with an FID detector, an autosampler, and a Varian 4290 integrating recorder. Either a 30 m x 0.25 mm DB-5, DB-17, or DB-225 capillary column was used, depending on the specific compounds to be separated. Helium was the carrier gas. Melting points were measured with a Büchi melting point apparatus, using unsealed melting point capillary tubes. Melting points and boiling points are uncorrected. Nuclear magnetic resonance spectra were obtained using a Bruker AM-400 or Bruker AC-300 instrument, with chloroform-d_1 or benzene-d_6 as solvent.

Purification of Reagents

The purity of the reagents was determined by GC and was greater than 98% in all cases. In most cases, the purification methods were taken from Purification of Laboratory Chemicals.[126] Values for physical constants were obtained from the Handbook of Chemistry and Physics (CRC)[127] unless otherwise stated.

Purification of carbon tetrachloride. HPLC grade carbon tetrachloride (Aldrich) was used without further purification.

Purification of bromotrichloromethane. Commercial bromotrichloromethane was distilled at atmospheric pressure. The fraction boiling at 103-105°C was collected and stored over 4Å Linde molecular sieves.

Purification of benzene-d_6. Benzene-d_6 was purchased in 1.0 g vials. Individual vials were not stored after opening. No further purification was carried out.

Purification of benzene. Benzene was washed once with concentrated sulfuric acid and twice with a saturated sodium bicarbonate solution. It was dried with magnesium sulfate and distilled. The fraction boiling at 79-80°C (CRC 80.1°C) was stored over 4Å Linde molecular sieves.

Purification of cyclohexane. Cyclohexane was washed once with concentrated sulfuric acid and twice with a saturated sodium bicarbonate solution. It was dried with magnesium sulfate and distilled. The fraction boiling at 80-81°C (CRC 80.7°C) was stored over 4Å Linde molecular sieves.

Purification of chlorobenzene. Chlorobenzene was washed with concentrated sulfuric acid (until the acid layer was colorless) and twice with a saturated sodium bicarbonate solution. It was dried with magnesium sulfate and distilled. The fraction boiling at 131-132°C (CRC 132°C) was stored over 4Å Linde molecular sieves.

Purification of bromobenzene. Bromobenzene was washed with concentrated sulfuric acid (until the acid layer was colorless) and twice with a saturated sodium bicarbonate solution. It was dried with magnesium sulfate and distilled. The fraction boiling at 155-156°C (CRC 156°C) was stored over 4Å Linde molecular sieves.

Purification of benzyl chloride. Benzyl chloride was washed with concentrated sulfuric acid (until the acid layer was colorless) and twice with a saturated sodium bicarbonate solution. It was dried with magnesium sulfate and distilled under reduced pressure using a water aspirator (approximately 15 torr). The fraction boiling at 74-77°C (CRC 66°C at 11 torr) was stored over 4Å Linde molecular sieves.

Purification of diethyl ether. Ether was distilled from sodium metal immediately prior to use.

Purification of tetrahydrofuran (THF). THF was distilled from sodium metal

immediately prior to use.

Purification of triphenyltin hydride. Commercial triphenyltin hydride was stored in a desiccator in the freezer and used without further purification.

Purification of N-bromosuccinimide. N-bromosuccinimide was recrystalized from boiling water. The crystals were dried under vacuum. M.p. 179-181°C, (lit. 183-184°C).[126]

Purification of azobisisobutyronitrile (AIBN). Commercial AIBN was recrystalized from chloroform by the addition of petroleum ether (b.p. 30-60°C). It was stored in the refrigerator in a brown glass bottle. M.p. 101.5-102°C with decomposition (lit. 103°C).[126]

Purification of toluene. Toluene was washed once with concentrated sulfuric acid and twice with a saturated sodium bicarbonate solution. It was dried with magnesium sulfate and distilled. The fraction boiling at 110-111°C (CRC 110.6°C) was used.

Purification of ethylbenzene. Ethylbenzene was washed once with concentrated sulfuric acid and twice with a saturated sodium bicarbonate solution. It was dried with magnesium sulfate and distilled. The fraction boiling at 134-135°C (CRC 136.2°C) was stored over 4Å Linde molecular sieves.

Purification of cumene. Cumene was distilled. The fraction boiling at 152-154°C (CRC 152.4°C) was used.

Purification of anisole. Anisole was distilled. The fraction boiling at 154-155°C (CRC 155°C) was used.

Purification of *p*-xylene. *p*-Xylene was washed with concentrated hydrochloric acid (until the acid layer was colorless) and twice with a saturated solution of sodium bicarbonate. It was dried with magnesium sulfate and distilled. The fraction boiling at 137.5-138.5°C (CRC 138.3°C) was used.

Purification of *m*-xylene. *m*-Xylene was washed with concentrated hydrochloric acid (until the acid layer was colorless) and twice with a saturated solution of sodium bicarbonate. It was dried with magnesium sulfate and distilled. The fraction boiling at 138-139°C (CRC 139.1°C) was used.

Purification of 4-methoxytoluene. 4-Methoxytoluene was distilled. The fraction boiling at 172-173°C (CRC 176.5°C) was stored over 4Å sieves.

Purification of 3-chlorotoluene. 3-Chlorotoluene was distilled. The fraction boiling at 159-161°C (CRC 162°C) was used.

Purification of 4-chlorotoluene. 4-Chlorotoluene was distilled. The fraction boiling at 159-160°C (CRC 162°C) was used.

Purification of 4-cyanotoluene. 4-Cyanotoluene was distilled. The fraction boiling at 210-215°C (CRC 217.6°C) was used.

Purification of 4-*tert*-butyltoluene. 4-*tert*-Butyltoluene was found to be >98% pure by GC and it was used without further purification.

Purification of *sec*-butylbenzene. *sec*-Butylbenzene was found to be >98% pure by GC and it was used without further purification.

Purification of 3-phenylpentane. 3-Phenylpentane was found to be >98% pure by GC and it was used without further purification.

Purification of *n*-propylbenzene. *n*-Propylbenzene was found to be >98% pure by GC and it was used without further purification.

Purification of *iso*butylbenzene. *Iso*butylbenzene was found to be >98% pure by GC and it was used without further purification.

Purification of propylene oxide. Commercial propylene oxide (Aldrich, 99+% purity) was used without further purification.

Purification of epichlorohydrin. Commercial epichlorohydrin (Aldrich, 99+% purity) was used without further purification.

Purification of cyclohexyl chloride. Cyclohexyl chloride was distilled. The fraction boiling at 142-143°C (CRC 143°C) was used.

Purification of neophyl chloride. Neophyl chloride was distilled at reduced pressure (approx. 12-15 torr) using a water aspirator. The fraction boiling at 107-110°C (lit. 95-96°C/10 torr) was used.

Purification of *m*-CPBA. 80-85% *m*-CPBA (Aldrich) was used without further purification.

Purification of Vitride. Vitride (Hexcel, 70% solution in toluene) was used without further purification.

Purification of 1,1-dichloroacetone. Commercial 1,1-dichloroacetone (Aldrich, 98%) was used without further purification.

Purification of cyclopropyl bromide. Commercial cyclopropyl bromide (Aldrich, 99%) was distilled. The fraction boiling at 68-69° (lit. 69°C) was used.[95]

Purification of acrolein. Commercial acrolein (Aldrich, 97%) was distilled immediately prior to use. The fraction boiling at 52-54°C (CRC 52.5-53.5°C) was used.

Purification of thiocarbonyldiimidazole. Commercial thiocarbonyldiimidazole (Aldrich, 90%) was stored in the freezer and used without further purification.

Purification of 4-N,N-dimethylaminopyridine (DMAP). Commercial DMAP (Aldrich, 99+%) was used without further purification.

Purification of 2-bromopyridine. Commercial 2-bromopyridine (Aldrich, 99%) was used without further purification.

Purification of trichloroacetyl chloride. Commercial trichloroacetyl chloride (Aldrich, 99%) was used without further purification.

Purification of *p*-toluidine. *p*-Toluidine was recrystalized from boiling water.

Drying under vacuum. gave white crystals, m.p. 39-45°C (CRC 44-45°C).

Purification of 3-bromobenzotrifluoride. Commercial 3-bromobenzotrifluoride (Aldrich, 99%) was used without further purification.

Preparation of Compounds

Preparation of trichloroiodomethane. A two fold excess of sodium iodide in acetone was added to a solution of bromotrichloromethane in acetone at 54°C. The reaction was stirred for 35 minutes. Attempts to isolate trichloroiodomethane by filtration of sodium bromide and subsequent reduced pressure distillation of the filtrate after removal of the solvent were unsuccessful. Decomposition to form iodine and hexachloroethane was apparently too rapid.

Preparation of trichloroacetyl peroxide. Preparation of the bis(trichloroacetyl) peroxide was attempted by the method of Loken *et al.*[48] To a brine solution made up of 6 g of sodium chloride, 30 ml of water and containing 1.4 g of sodium peroxide was added 2.75 ml of trichloroacetyl chloride. The reaction was kept below -10°C by a dry ice / carbon tetrachloride bath. After thirty minutes, 10 ml of methylene chloride was added and stirring was stopped. The methylene chloride layer was removed and stored in the freezer.

Attempts to decompose the peroxide solution in the presence of cumene showed no evidence for hydrogen atom abstraction. In fact, the half-life of the peroxide is only about 10 minutes[49] in solution at 0°. This low stability makes the peroxide useless as a source of trichloromethyl radicals for the study of benzylic hydrogen atom abstraction.

Preparation of *tert*-butyl trichloroperacetate. Preparation of *tert*-butyl trichloroperacetate was accomplished by the method of Leffler and Gibson.[49] To a solution of trichloroacetyl chloride in hexane was added 1.1 equivalents of *tert*-butyl

hydroperoxide and 1.1 equivalents of pyridine. The reaction mixture was stirred at 0° for 2 hours, during which the formation of pyridinium chloride was observed. After 2 hours, the reaction mixture was poured over 30 g of ice. The hexane layer was washed twice with 7% hydrochloric acid and twice with saturated sodium bicarbonate solution. The hexane layer was dried with magnesium sulfate and the solvent was removed under vacuum. The product was a clear colorless oil. The carbonyl band in the IR was 1798 cm^{-1} (1795 cm^{-1} reported).[49]

Preparation of the 2-bromopyridine-N-oxide hydrochloride salt. Oxidation of 2-bromopyridine (20 g, 0.126 moles) with *m*-CPBA (30 g) in chloroform was carried out at room temperature for 4 days. The reaction mixture was then washed with three 50 ml portions of 20% hydrochloric acid. The combined aqueous layers were evaporated to dryness under vacuum. The residue was dissolved in ether. Filtration and removal of solvent yielded 8.0 g (30%) of 2-bromopyridine-N-oxide hydrochloride salt, m.p. 120-124°C (reported 130-135°C).[53]

Preparation of sodium 2-pyridinthione-N-oxide. A solution of 8.0 g of 2-bromopyridine-N-oxide hydrochloride salt in water was added slowly to a refluxing solution of sodium sulfide in water over the course of 30 minutes. The reaction mixture was then refluxed for an additional hour. Filtration and acidification with 20% hydrochloric acid caused the formation of a precipitate. The solid was recrystalized from ethanol to give 2.7 g (39%) of sodium 2-pyridinthione-N-oxide. Subsequent treatment of this salt with trichloroacetyl chloride gave only decomposition even at -10°C in the dark.[53]

Preparation of 3,5-dibromotoluene. A solution of 50 g (0.467 moles) of *p*-toluidine in 700 ml of glacial acetic acid was prepared. This solution was stirred at room temperature and bromine was added dropwise until a cloudy yellow color persisted. The mixture was then diluted with 50 ml of cold water and filtered to give

crude 2,6-dibromotoluidine which was carried on to the next step without further purification.

The crude 2,6-dibromotoluidine was dissolved in 500 ml of 100% ethanol containing 50 ml of concentrated sulfuric acid and 50 g of sodium nitrite. This reaction mixture was refluxed for 4 hours. Cooling and dilution with water gave 6.2 g of orange crystals, m.p. 32-34°. Two recrystalizations from methanol/water (10:1) and drying in a desiccator gave 5.3 g (5% overall yield for both steps) of beige crystals, m.p. 35-36°C (reported 36.8-37.0°C).[128] ^{1}H NMR (300 MHz, $CDCl_3$): 7.47 (1H, s), 7.26 (2H, s), 2.31 (3H, s, methyl group).

Preparation of *m*-trifluoromethyltoluene. A solution of 1.2 g of 3-bromobenzotrifluoride in 5.0 ml of ether was cooled with stirring to -100°C (dry ice/ether bath). To this was slowly added 5.5 ml of a 1.0 M solution of methyl lithium in ether. Upon addition of methyl lithium, the reaction turned yellow and then the color faded. After 10 minutes at -100°, the reaction was allowed to warm to 0°C and a sample was analyzed by GC. This analysis showed that the reaction had gone to completion. Fractional distillation gave 0.8 g of pure *m*-trifluoromethyltoluene, b.p. 125-127°C (reported 127°C).[129] ^{1}H NMR (300 MHz, $CDCl_3$): 7.40 (4H, m), 2.41 (3H, s, methyl group).

Preparation of *neo*pentylbenzene. A Grignard reagent was prepared by adding 14.0 ml (0.133 moles) of bromobenzene slowly to 80 ml of ether containing 13 g (3 equivalents) of magnesium turnings. After the addition was complete, the reaction mixture was refluxed for 2 hours.

The phenylmagnesium bromide solution was then added slowly to a cooled solution containing 10.2 ml (0.083 moles) of pivoyl chloride in 50 ml of ether so as to prevent the temperature from rising above 10°C. After addition was complete, the reaction was quenched with water and washed twice with 10% hydrochloric acid

solution. Drying of the organic layer with magnesium sulfate, removal of the solvent under vacuum, and reduced pressure distillation gave 4.16 g (31%) of phenyl *tert*-butyl ketone, n_D=1.5131 (reported n_D=1.5102).[130]

A mixture of 4.0 g (0.025 moles) of phenyl *tert*-butyl ketone, 3.0 ml of hydrazine monohydrate, and 4.0 g of potassium hydroxide in 50 ml of diethylene glycol were refluxed for 6 hours. Neutralization with dilute hydrochloric acid and distillation gave 0.90 g (25%) *neo*pentylbenzene, n_D=1.4894 (reported n_D=1.4888), b.p. 183-185°C (reported 185-186°C).[131]

Preparation of *tert*-butyl hypochlorite. The method of Walling and Mintz was used to prepare *tert*-butyl hypochlorite. Purex® bleach (500 ml) was cooled to 0°C. Mechanical stirring was used and the lights in the hood were turned off in order to prevent decomposition of the product as it formed. To the stirred bleach was added 37 ml of glacial acetic acid and 24.5 ml of *tert*-butyl alcohol. Vigorous stirring was continued for 3-5 minutes. The reaction mixture was then washed with 50 ml of a saturated sodium bicarbonate solution and then 50 ml of water. The yellow organic layer (20-25 g, ≈70%) was dried with magnesium sulfate and used without further purification.

Preparation of 2-chloroepoxypropanes. Freshly prepared *tert*-butyl hypochlorite was used in the photochlorination of propylene oxide. A mixture of propylene oxide and *tert*-butyl hypochlorite in a molar ratio of 3:1 was irradiated at 0°C until the yellow color had disappeared and then for an additional half-hour. Preparative GC was used to collect the three new products. The major product (75%) was identified as 2-chloro-1,2-epoxypropane, ^{1}H NMR (300 MHz, $CDCl_3$): 3.10 (1H, d, J=4.9 Hz), 2.83 (1H, d, J=4.9 Hz), 1.89 (3H, s, CH_3).

Preparation of *trans*- and *cis*-1-chloro-1,2-epoxypropane. A solution containing 7.0 g of 1,1-dichloroacetone in 5 ml of toluene was cooled to 0°C. To this

was added 1.1 equivalents of Vitride at a rate which maintained a temperature below 10°C. The reaction mixture was stirred for an additional hour at 0°C before warming to room temperature. The reaction was quenched slowly with water and the toluene layer was washed with a sodium bicarbonate solution and dried with magnesium sulfate. Distillation gave 6.4 g (90%) of 1,1-dichloro-2-propanol, b.p. 140-150°C.

Vigorous shaking of a benzene solution of 1,1-dichloro-2-propanol with a saturated sodium hydroxide solution gave complete conversion to *trans*- and *cis*-1-chloro-1,2-epoxypropane. ^{1}H NMR(trans) (300 MHz, $CDCl_3$): 4.82 (1H, d, *J*=1.0 Hz), 3.22 (1H, dq, *J*=1.0 and 5.2 Hz) 1.36 (3H, d, *J*=5.2 Hz). ^{1}H NMR(cis) (300 MHz, $CDCl_3$): 5.16 (1H, d, *J*=2.8 Hz), 3.18 (1H, dq, *J*=2.8 and 5.4 Hz), 1.49 (3H, d, *J*=5.4 Hz).

Preparation of *erythro*- and *threo*-3-chloro-1,2-epoxybutane. Epoxidation of 3-chloro-1-butene with *m*-CPBA in refluxing methylene chloride for 12 hours gave a 1:1 mixture of the erythro and threo compounds. Isolation of each isomer was accomplished by preparative GC. ^{1}H NMR(erythro) (300 MHz, $CDCl_3$): 3.64 (1H, p, *J*=6.7 Hz), 3.08 (1H, m), 2.88 (1H, t, *J*=4.2 Hz), 2.69 (1H, dd, *J*=4.7 and 2.5 Hz), 1.61 (3H, d, *J*=6.6). ^{13}C NMR(erythro) (75.5 MHz, $CDCl_3$): 56.8, 55.5, 47.2, 21.8. ^{1}H NMR(threo) (300 MHz, $CDCl_3$): 3.80 (1H, p, *J*=6.7 Hz), 3.15 (1H, m), 2.89 (1H, dd, *J*=4.7 and 4.0), 2.72 (1H, dd, *J*=4.8 and 2.5), 1.55 (3H, d, *J*=6.7 Hz). ^{13}C NMR(threo) (75.5 MHz, $CDCl_3$): 57.6, 55.7, 46.4, 20.6.

Preparation of 3-chlorocyclohexene. Photoinitiated chlorination of cyclohexene using *tert*-butyl hypochlorite was carried out by the method of Walling *et al.*[132]

Preparation of *trans*- and *cis*-2-chloro-7-oxabicyclo[4.1.0]heptane. Epoxidation of 3-chlorocyclohexene with *m*-CPBA in refluxing methylene chloride for 12 hours gave a 9:1 mixture of compounds. Separation and isolation of each isomer

was accomplished by preparative GC. ^{1}H NMR (major isomer) (300 MHz, $CDCl_3$): 4.35 (1H, t, *J*=4.8), 3.29 (1H, d, *J*=4.2), 3.25 (1H, t, *J*=3.4), 1.96 (3H, m), 1.60 (2H, m), 1.32 (1H, m). ^{13}C NMR (major isomer) (75.5 MHz, $CDCl_3$): 55.0, 54.9, 52.2, 28.8, 23.1, 15.1. HRMS (calc. for $^{12}C_6{}^{1}H_9{}^{16}O_1{}^{35}Cl_1$: 132.03419, found: 132.03419). ^{1}H NMR (minor isomer) (300 MHz, $CDCl_3$): 4.27 (1H, ddd, *J*=10.0, 5.3, and 1.9), 3.32 (2H, m), 1.70 (5H, m), 1.27 (1H, m). ^{13}C NMR (minor isomer) (75.5 MHz, $CDCl_3$): 57.4, 56.5, 55.3, 29.4, 22.3, 20.7. HRMS (calc. for $^{12}C_6{}^{1}H_9{}^{16}O_1{}^{35}Cl_1$: 132.03419, found: 132.03419).

Treatment of each isomer with an equivalent of conc. HCl gave a single isomer of 2,6-dichlorocyclohexanol. The major isomer gave only *trans, trans*-2,6-dichlorocyclohexanol, ^{1}H NMR (300 MHz, $CDCl_3$): 3.73 (2H, m), 3.58 (1H, t, *J*=9.5), 3.00 (1H, broad s, OH), 2.22 (2H, m), 1.85 (1H, m), 1.72 (2H, m), 1.39 (1H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$): 79.8, 62.8, 34.7, 23.9. Similar treatment of the minor isomer gave only *trans, cis*-2,6-dichlorocyclohexanol, ^{1}H NMR (300 MHz, $CDCl_3$) 4.55 (1H, m), 4.29 (1H, m), 3.78 (1H, m), 2.55 (1H, broad s, OH), 2.25 (1H, m), 2.05 (1H, m), 1.77 (4H, mm). ^{13}C NMR (75.5 MHz, $CDCl_3$): 74.8, 62.4, 60.1, 31.5, 19.8.

Preparation of 1-cyclopropyl-2-propen-1-ol. A solution of 20 g (0.164 moles) of cyclopropyl bromide in 20 ml of ether was added dropwise to 100 ml of ether at 0°C, containing 5.0 g (4 equivalents) of lithium wire.[95] Addition was such that the temperature did not rise above 10°C. After addition, the reaction was stirred for another 2 hours at 0°C.

The cyclopropyl lithium solution was then transferred to an addition funnel and added dropwise to 9.2 g (0.164 moles) of acrolein in 100 ml of ether at -78°C (dry ice / acetone bath). The rate of addition was sufficiently slow that the temperature remained below -20°C. Once addition was complete, the reaction was allowed to warm slowly to

room temperature. The reaction mixture was then poured over ice and the ether layer was washed twice with water, and dried with magnesium sulfate. Solvent removal under vacuum. and reduced pressure distillation gave 8.9 g (56%) of 1-cyclopropyl-2-propen-1-ol. ^{1}H NMR (300 MHz, $CDCl_3$): 5.98 (1H, ddd, J=17.3, 10.5, and 5.4), 5.25 (1H, d, J=17.2), 5.11 (1H, d, J=10.5), 3.49 (1H, dd, J=5.4 and 7.4), 1.98 (1H, broad s, OH), 1.00 (1H, m), 0.55 (2H, m), 0.30 (2H, m). ^{13}C NMR (75.5 MHz, C_6D_6): 140.6, 113.8, 76.3, 17.6, 2.9, 2.0.

Preparation of 1-cyclopropyl-2-propen-1-one. Oxidation of 1-cyclopropyl-2-propen-1-ol with 4-6 equivalents of manganese dioxide[96] in chloroform at room temperature gave 1-cyclopropyl-2-propen-1-one. The reaction was run for between 4 and 6 days and followed by ^{1}H NMR. Filtration and solvent removal gave low isolated yields (typically 15-20%) of the ketone. ^{1}H NMR (300 MHz, $CDCl_3$): 6.48 (1H, dd), 6.29 (1H, dd), 5.83 (1H, dd), 2.21 (1H, m), 1.12 (2H, m), 0.96 (2H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$): 200.5, 136.6, 127.5, 18.2, 11.2.

Preparation of 1-cyclopropyl-2,3-epoxy-1-propanol. Oxidation of 1.0 g of 1-cyclopropyl-2-propen-1-ol with 7.0 g (4 equivalents) of *m*-CPBA in 35 ml of refluxing chloroform gave 0.54 g (45%) of a ≈1:1 mixture of diastereomeric epoxyalcohols. ^{1}H NMR (300 MHz, $CDCl_3$): 3.1 (3H, mm), 2.9-2.7 (5H, mm), 2.52 (1H, broad s, OH, int. 1.0), 2.39 (1H, broad s, OH, int. 1.0), 1.09 (1H, m, cyclopropyl methine, int. 1.2), 0.93 (1H, m, cyclopropyl methine from other diastereomer, int. 1.2), 0.59 (4H, mm), 0.42-0.25 (4H, mm). ^{13}C NMR (75.5 MHz, $CDCl_3$): 75.4, 73.2, 54.9, 54.0, 44.8, 43.4, 14.3, 13.2, 2.4, 2.1, 1.7, 1.6.

Preparation of 1-cyclopropyl-2,3-epoxy-1-propanone. A solution of 0.73 g (7.6 mmoles) of 1-cyclopropyl-2-propen-1-one in 3.8 ml of methanol containing 2.2 ml of 30% hydrogen peroxide was prepared and cooled to 0°C in an ice bath. To this was added dropwise 1.9 ml of aqueous 2.0 M sodium hydroxide over a 30 minute period.

Following addition, the reaction was stirred for 1 hour. Extraction of the reaction mixture with ether and solvent removal gave 0.69 g (80%) of 1-cyclopropyl-2,3-epoxy-1-propanone. ^{1}H NMR (300 MHz, $CDCl_3$): 3.48 (1H, m), 3.03 (1H, m), 2.97 (1H, m), 2.02 (1H, m), 1.10 (2H, m), 0.93 (2H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$): 207.4, 53.6, 45.8, 14.6, 12.0, 11.4.

Preparation of zinc borohydride. A slurry of 4.0 g of zinc chloride in 50 ml of ether was boiled until most of the solid had dissolved. The solution was filtered and added dropwise at room temperature to a stirred suspension of 2.7 g of sodium borohydride in 150 ml of ether. The reaction mixture was stirred for 5 hours at room temperature, then cooled. The ethereal solution of approximately 0.2 M zinc borohydride was poured off from the sodium chloride which had precipitated, and used without further purification.[98a]

Preparation of *erythro*-1-cyclopropyl-2,3-epoxy-1-propanol. A solution of 90 mg (0.80 mmoles) of 1-cyclopropyl-2,3-epoxy-1-propanone in 5.0 ml of ether was treated with 3.0 ml of zinc borohydride in ether at -5°C (ice / acetone bath) for 1 hour. The reaction was then quenched with 2 ml of water and stirred for an additional 30 minutes at room temperature. Extraction with ether and solvent removal gave 54 mg (60%) of 1-cyclopropyl-2,3-epoxy-1-propanol with an erythro : threo ratio of 97:3 by ^{13}C NMR line heights. ^{1}H NMR (300 MHz, $CDCl_3$): 3.09 (2H, m), 2.81 (1H, dd), 2.71 (1H, dd), 0.85 (1H, m), 0.51 (2H, m), 0.30 (2H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$): 73.2, 54.0, 43.4, 13.2, 2.2, 1.6.

Preparation of thioimidazolide from 1-cyclopropyl-2,3-epoxy-1-propanol. A mixture of 54 mg (0.47 mmoles) of *erythro*-1-cyclopropyl-2,3-epoxy-1-propanol, 90 mg (0.50 mmoles) of thiocarbonyldiimidazole, and 6 mg (0.05 mmoles) of DMAP in 3.0 ml of chloroform was stirred for 12 hours at room temperature.[84] The reaction mixture was washed twice with a sodium bicarbonate solution and twice with water.

The organic layer was dried with magnesium sulfate and the solvent was removed under vacuum leaving 73 mg (70%) of >98% pure thioimidazolide. ^{1}H NMR (300 MHz, C_6D_6): 8.30 (1H, s), 7.36 (1H,), 6.88 (1H,), 4.97 (1H, dd, *J*=9.4 and 3.6), 2.79 (1H, m), 2.32 (1H, m), 2.18 (1H, m), 0.83 (1H,), 0.23 (2H, m), 0.16 (2H, m). ^{13}C NMR (75.5 MHz, C_6D_6): 184.5, 136.9, 131.5, 118.3, 87.0, 51.1, 44.2, 10.4, 3.3, 2.6.

Kinetic Methods

Photoinitiated reactions of bromotrichloromethane. Reaction mixtures contained a pair of substituted toluenes, an internal standard (either *p*-di-*tert*-butylbenzene or *p*-bromo-*tert*-butylbenzene), and bromotrichloromethane in an approximate molar ratio of 1:1:0.5:10. The reaction mixture was divided among several ampules which were sealed under a reduced pressure of nitrogen after three freeze-thaw cycles. In each case, one of the ampules was withheld for analysis of starting material concentrations. The remaining ampules were placed in a 70±0.5°C oil bath, just below the surface of the oil, and irradiated with a Ken-Rad 275-W sun lamp. Reaction times ranged from 2 to 5 hours.

AIBN-initiated reactions of bromotrichloromethane. Reaction mixtures contained a pair of substituted toluenes or a pair of unsubstituted alkylbenzenes, an internal standard (either *p*-di-*tert*-butylbenzene or *p*-bromo-*tert*-butylbenzene), AIBN, and bromotrichloromethane in an approximate molar ratio of 1:1:0.5:0.1:10. The reaction mixture was divided among several ampules which were sealed under a reduced pressure of nitrogen after three freeze-thaw cycles. In each case, one of the ampules was withheld for analysis of starting material concentrations. The remaining ampules wrapped in foil and placed in a 70±0.5°C oil bath. Reaction times ranged

from 48 to 336 hours.

Photoinitiated reactions of N-bromosuccinimide (NBS). Reaction mixtures contained a pair of toluenes, NBS, an internal standard, and carbon tetrachloride in an approximate molar ratio of 1:1:1:0.75:10. The reaction mixture was divided among several ampules which were sealed under a reduced pressure of nitrogen after three freeze-thaw cycles. In each case, one of the ampules was withheld for analysis of starting material concentrations. The remaining ampules were placed in a 70±0.5°C oil bath, just below the surface of the oil, and irradiated with a Ken-Rad 275-W sun lamp for 3 hours.

Reactions of chlorides with triphenyltin hydride. Reaction mixtures contained a pair of chlorides, an internal standard (anisole), triphenyltin hydride, AIBN, and solvent (either benzene-d_6 or cyclohexane) in an approximate molar ratio of 1:1:0.5:1:0.1:10. The reaction mixture was divided among several ampules which were sealed under a reduced pressure of nitrogen after three freeze-thaw cycles. In each case, one of the ampules was withheld for analysis of starting material concentrations. The remaining ampules wrapped in foil and placed in a 70±0.5°C oil bath. Reaction times ranged from 8 to 56 hours.

Reactions of ketones with triphenyltin hydride. Each ketone was studied individually. Reaction mixtures contained the α,β-epoxyketone, triphenyltin hydride, and benzene-d_6 in an approximate molar ratio of 0.2:1:5. The reaction mixture was divided among several ampules which were sealed under a reduced pressure of nitrogen after three freeze-thaw cycles. In each case, one of the ampules was withheld for analysis of starting material concentrations. The remaining ampules wrapped in foil

and placed in a 70±0.5°C oil bath. Reactions were run for exactly one hour. Products were determined by ^{1}H NMR spectroscopy.

Reactions of thioimidazolides with triphenyltin hydride. Reaction mixtures contained the thioimidazolide, triphenyltin hydride, AIBN, and benzene-d_6 in an approximate molar ratio of 1:7-19:0.05:10. The reaction mixture was divided among several ampules which were sealed under a reduced pressure of nitrogen after three freeze-thaw cycles. In each case, one of the ampules was withheld for analysis of starting material concentrations. The remaining ampules wrapped in foil and placed in a 70±0.5°C oil bath. In each run, the reaction was found to be complete within 30 minutes. The products were determined by ^{1}H NMR.

Calculation of Relative Rates

Relative rates were determined for pairs of reactants by monitoring the disappearance of each relative to an internal standard by ^{1}HNMR or GC. The standard formula for calculating relative rates was used (eq. 124).

$$\frac{k_y}{k_x} = \frac{\log (Y_i / Y_f)}{\log (X_i / X_f)} \qquad (124)$$

Y_i is the initial concentration of compound Y.
Y_f is the final concentration of compound Y.

X_i is the initial concentration of compound X.
X_f is the final concentration of compound X.

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Appendices

Appendix 1

Kinetic studies of the relative rates for reactions of substituted toluenes with bromotrichloromethane. Initiated with AIBN at 70°C.

Table 24. Relative rate of disappearance for *p*-methoxytoluene *vs. p*-xylene in bromotrichloromethane. AIBN initiated at 70°C for 120 hours.

Initial mmoles:					
	p-methoxytoluene	5.34	$BrCCl_3$	76	
	p-xylene	4.94	AIBN	1.22	
run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-methoxytoluene	3.09	2.25	42.1	1.65
	p-xylene	2.55	2.39	48.4	
2	*p*-methoxytoluene	3.17	2.17	40.6	1.72
	p-xylene	2.69	2.25	45.5	
3	*p*-methoxytoluene	3.21	2.13	39.9	1.63
	p-xylene	2.65	2.29	46.4	
4	*p*-methoxytoluene	3.01	2.33	43.6	1.97
	p-xylene	2.76	2.18	44.1	
5	*p*-methoxytoluene	3.13	2.21	41.4	1.63
	p-xylene	2.57	2.37	48.0	

Average $k_{rel} = 1.72 \pm 0.13$

Table 25. Relative rate of disappearance for *p*-*t*-butyltoluene *vs.* *p*-xylene in bromotrichloromethane. AIBN initiated at 70°C for 120 hours.

Initial mmoles:

p-*t*-butyltoluene	3.37	$BrCCl_3$	76
p-xylene	4.73	AIBN	1.43

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-*t*-butyltoluene	2.54	0.83	24.6	0.93
	p-xylene	2.58	2.15	45.5	
2	*p*-*t*-butyltoluene	2.32	1.05	31.2	1.07
	p-xylene	2.36	2.37	50.1	
3	*p*-*t*-butyltoluene	2.48	0.89	26.4	0.93
	p-xylene	2.45	2.28	48.2	
4	*p*-*t*-butyltoluene	2.50	0.87	25.8	0.99
	p-xylene	2.58	2.15	45.5	
5	*p*-*t*-butyltoluene	2.57	0.80	23.7	0.91
	p-xylene	2.60	3.13	45.0	

Average $k_{rel} = 0.97 \pm 0.06$

Table 26. Relative rate of disappearance for *m*-xylene *vs.* *p*-chlorotoluene in bromotrichloromethane. AIBN initiated at 70°C for 120 hours.

Initial mmoles:

m-xylene	4.65	$BrCCl_3$	77
p-chlorotoluene	4.03	AIBN	1.22

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*m*-xylene	2.94	1.71	36.8	1.01
	p-chlorotoluene	3.21	0.82	20.3	
2	*m*-xylene	2.83	1.82	39.1	1.09
	p-chlorotoluene	3.21	0.82	20.3	
3	*m*-xylene	2.96	1.69	36.3	0.99
	p-chlorotoluene	3.21	0.82	20.3	
4	*m*-xylene	2.91	1.74	37.4	0.98
	p-chlorotoluene	3.17	0.86	21.3	
5	*m*-xylene	2.91	1.74	37.4	1.03
	p-chlorotoluene	3.21	0.82	20.3	

Average $k_{rel} = 1.02 \pm 0.04$

Table 27. Relative rate of disappearance for *p*-chlorotoluene *vs.* *p*-xylene in bromotrichloromethane. AIBN initiated at 70°C for 120 hours.

Initial mmoles:

p-chlorotoluene	4.32	$BrCCl_3$	76
p-xylene	4.79	AIBN	1.22

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-chlorotoluene	3.48	0.84	19.4	0.74
	p-xylene	2.68	2.11	44.1	
2	*p*-chlorotoluene	3.50	0.82	19.0	0.61
	p-xylene	2.41	2.38	49.7	
3	*p*-chlorotoluene	3.46	0.86	19.9	0.63
	p-xylene	2.36	2.43	50.7	
4	*p*-chlorotoluene	3.48	0.84	19.4	0.74
	p-xylene	2.67	2.12	44.3	

Average $k_{rel} = 0.68 \pm 0.06$

Table 28. Relative rate of disappearance for *m*-chlorotoluene *vs.* *p*-xylene in bromotrichloromethane. AIBN initiated at 70°C for 140 hours.

Initial mmoles:

m-chlorotoluene	3.98	$BrCCl_3$	77
p-xylene	5.90	AIBN	1.22

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*m*-chlorotoluene	3.49	0.49	12.3	0.45
	p-xylene	3.28	2.62	44.4	
2	*m*-chlorotoluene	3.51	0.47	11.8	0.45
	p-xylene	2.41	2.38	49.7	
3	*m*-chlorotoluene	3.51	0.47	11.8	0.44
	p-xylene	3.32	2.58	43.7	
4	*m*-chlorotoluene	3.47	0.51	12.8	0.46
	p-xylene	3.26	2.64	44.7	
5	*m*-chlorotoluene	3.49	0.49	12.3	0.46
	p-xylene	3.32	2.58	43.7	

Average $k_{rel} = 0.45 \pm 0.01$

Table 29. Relative rate of disappearance for *m*-trifluoromethyltoluene *vs.* *p*-chlorotoluene in bromotrichloromethane. AIBN initiated at 70°C for 240 hours.

Initial mmoles:

m-CF_3-toluene	0.95	$BrCCl_3$	20
p-chlorotoluene	1.84	AIBN	0.39

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*m*-CF_3-toluene	0.61	0.34	35.8	0.63
	p-chlorotoluene	0.91	0.93	50.5	
2	*m*-CF_3-toluene	0.57	0.38	40.0	0.74
	p-chlorotoluene	0.92	0.92	50.0	
3	*m*-CF_3-toluene	0.64	0.31	32.6	0.54
	p-chlorotoluene	0.89	0.95	51.6	
4	*m*-CF_3-toluene	0.52	0.43	45.3	0.94
	p-chlorotoluene	0.97	0.87	47.3	

Average $k_{rel} = 0.71 \pm 0.15$

Table 30. Relative rate of disappearance for *p*-cyanotoluene *vs.* *p*-chlorotoluene in bromotrichloromethane. AIBN initiated at 70°C for 240 hours.

Initial mmoles:

p-cyanotoluene	4.27	$BrCCl_3$	76
p-chlorotoluene	4.30	AIBN	2.84

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-cyanotoluene	3.91	0.36	8.4	0.42
	p-chlorotoluene	3.49	0.81	18.8	
2	*p*-cyanotoluene	3.94	0.33	7.7	0.34
	p-chlorotoluene	3.40	0.90	20.9	
3	*p*-cyanotoluene	3.63	0.64	15.0	0.59
	p-chlorotoluene	3.27	1.03	24.0	
4	*p*-cyanotoluene	3.71	0.56	13.1	0.58
	p-chlorotoluene	3.38	0.92	21.4	
5	*p*-cyanotoluene	3.69	0.58	13.6	0.61
	p-chlorotoluene	3.38	0.92	21.4	

Average $k_{rel} = 0.51 \pm 0.11$

Table 31. Relative rate of disappearance for 3,5-dibromotoluene *vs.* *p*-chlorotoluene in bromotrichloromethane. AIBN initiated at 70°C for 168 hours.

Initial mmoles:					
	3,5-dibromotoluene	0.81	$BrCCl_3$	25	
	p-chlorotoluene	1.60	AIBN	0.33	
run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	3,5-dibromotoluene	0.76	0.05	6.2	0.53
	p-chlorotoluene	1.42	0.18	11.3	
2	3,5-dibromotoluene	0.72	0.09	11.1	0.64
	p-chlorotoluene	1.33	0.27	16.9	
3	3,5-dibromotoluene	0.72	0.09	11.1	0.61
	p-chlorotoluene	1.32	0.28	17.5	
4	3,5-dibromotoluene	0.72	0.09	11.1	0.61
	p-chlorotoluene	1.32	0.28	17.5	
5	3,5-dibromotoluene	0.73	0.08	9.9	0.64
	p-chlorotoluene	1.36	0.24	15.0	

Average $k_{rel} = 0.61 \pm 0.04$

Table 32. Relative rate of disappearance for anisole *vs.* *p*-xylene in bromotrichloromethane. AIBN initiated at 70°C for 120 hours.

Initial mmoles:

anisole	4.80	$BrCCl_3$	76
p-xylene	5.50	AIBN	1.05

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	anisole	4.03	0.77	16.0	0.40
	p-xylene	2.29	3.21	58.4	
2	anisole	3.87	0.93	19.4	0.52
	p-xylene	2.39	3.11	56.5	
3	anisole	4.17	0.63	13.1	0.37
	p-xylene	2.57	2.93	53.3	
4	anisole	4.28	0.52	10.8	0.34
	p-xylene	2.81	2.69	48.9	

Average $k_{rel} = 0.41 \pm 0.07$

Appendix 2

Kinetic studies of the relative rates for reactions of substituted toluenes with bromotrichloromethane. Photoinitiated at 70°C.

Table 33. Relative rate of disappearance for *p*-methoxytoluene *vs.* *p*-xylene in bromotrichloromethane. Photoinitiated at 70°C for 1.75 hours.

Initial mmoles:
p-methoxytoluene 4.85 $BrCCl_3$ 94
p-xylene 4.77

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-methoxytoluene	0.60	4.25	87.6	2.42
	p-xylene	0.85	3.92	82.2	
2	*p*-methoxytoluene	1.13	3.72	76.7	2.52
	p-xylene	1.50	3.27	68.6	
3	*p*-methoxytoluene	0.88	3.97	81.9	2.33
	p-xylene	1.10	3.67	76.9	
4	*p*-methoxytoluene	1.49	3.36	69.3	2.41
	p-xylene	1.79	2.98	62.5	
5	*p*-methoxytoluene	1.28	3.57	73.6	2.36
	p-xylene	1.54	3.23	67.7	
6	*p*-methoxytoluene	1.31	3.54	73.0	2.44
	p-xylene	1.63	3.14	65.8	

Average $k_{rel} = 2.41 \pm 0.06$

Table 34. Relative rate of disappearance for *p*-*t*-butyltoluene *vs.* *p*-xylene in bromotrichloromethane. Photoinitiated at 70°C for 2.5 hours.

Initial mmoles:
p-*t*-butyltoluene 3.51 $BrCCl_3$ 76
p-xylene 4.80

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-*t*-butyltoluene	1.45	2.06	58.7	1.03
	p-xylene	0.86	3.94	82.1	
2	*p*-*t*-butyltoluene	1.36	2.15	61.3	0.95
	p-xylene	0.65	4.15	86.5	
3	*p*-*t*-butyltoluene	1.28	2.23	63.5	0.92
	p-xylene	0.54	4.26	88.8	
4	*p*-*t*-butyltoluene	1.62	1.89	53.8	1.02
	p-xylene	1.06	3.74	77.9	
5	*p*-*t*-butyltoluene	1.26	2.25	64.1	0.90
	p-xylene	0.49	4.31	89.8	
6	*p*-*t*-butyltoluene	1.24	2.27	64.7	0.93
	p-xylene	0.51	4.29	89.4	

Average $k_{rel} = 0.96 \pm 0.05$

Table 35. Relative rate of disappearance for *m*-xylene *vs.* *p*-chlorotoluene in bromotrichloromethane. Photoinitiated at 70°C for 2.5 hours.

Initial mmoles:
m-xylene 4.77 $BrCCl_3$ 76
p-chlorotoluene 4.08

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*m*-xylene	3.45	1.32	27.7	1.02
	p-chlorotoluene	3.48	0.60	14.7	
2	*m*-xylene	2.73	2.04	42.8	1.11
	p-chlorotoluene	3.17	0.91	22.3	
3	*m*-xylene	2.75	2.02	42.3	1.09
	p-chlorotoluene	3.17	0.91	22.3	
4	*m*-xylene	3.30	1.47	30.8	0.96
	p-chlorotoluene	3.37	0.71	17.4	

Average $k_{rel} = 1.04 \pm 0.06$

Table 36. Relative rate of disappearance for *p*-chlorotoluene *vs.* *p*-xylene in bromotrichloromethane. Photoinitiated at 70°C for 2.5 hours.

Initial mmoles:
p-chlorotoluene 3.99 $BrCCl_3$ 77
p-xylene 6.59

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-chlorotoluene	3.60	0.39	9.8	0.58
	p-xylene	4.62	1.97	29.9	
2	*p*-chlorotoluene	3.62	0.37	9.3	0.58
	p-xylene	4.72	1.87	28.4	
3	*p*-chlorotoluene	3.89	0.10	2.5	0.50
	p-xylene	5.95	0.64	9.7	
4	*p*-chlorotoluene	3.77	0.22	5.5	0.46
	p-xylene	5.16	1.43	21.7	
5	*p*-chlorotoluene	2.57	1.42	35.6	0.56
	p-xylene	1.38	5.12	79.1	

Average $k_{rel} = 0.54 \pm 0.05$

Table 37. Relative rate of disappearance for *m*-chlorotoluene *vs.* *p*-xylene in bromotrichloromethane. Photoinitiated at 70°C for 2.5 hours.

Initial mmoles:
m-chlorotoluene 4.13 $BrCCl_3$ 76
p-xylene 9.04

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*m*-chlorotoluene	2.50	1.63	39.5	0.42
	p-xylene	0.85	8.19	90.6	
2	*m*-chlorotoluene	2.43	1.70	41.2	0.35
	p-xylene	0.45	8.59	95.0	
3	*m*-chlorotoluene	2.54	1.59	38.5	0.39
	p-xylene	0.73	8.31	91.9	
4	*m*-chlorotoluene	2.28	1.85	44.8	0.42
	p-xylene	0.54	8.50	94.0	
5	*m*-chlorotoluene	2.57	1.56	37.8	0.48
	p-xylene	1.24	7.80	86.3	
6	*m*-chlorotoluene	2.32	1.81	43.8	0.46
	p-xylene	0.75	8.29	91.7	

Average $k_{rel} = 0.42 \pm 0.04$

Table 38. Relative rate of disappearance for *m*-trifluoromethyltoluene *vs.* *p*-chlorotoluene in bromotrichloromethane. Photoinitiated at 70°C for 8.0 hours.

Initial mmoles:
m-CF_3-toluene 1.01 $BrCCl_3$ 20
p-chlorotoluene 1.58

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*m*-CF_3-toluene	0.95	0.06	5.9	0.54
	p-chlorotoluene	1.41	0.17	10.8	
2	*m*-CF_3-toluene	0.97	0.04	4.0	0.44
	p-chlorotoluene	1.44	0.14	8.9	
3	*m*-CF_3-toluene	0.86	0.15	14.9	0.44
	p-chlorotoluene	1.10	0.48	30.4	
4	*m*-CF_3-toluene	0.83	0.18	17.8	0.40
	p-chlorotoluene	0.97	0.61	38.6	

Average $k_{rel} = 0.45 \pm 0.05$

Table 39. Relative rate of disappearance for *p*-cyanotoluene *vs.* *p*-chlorotoluene in bromotrichloromethane. Photoinitiated at 70°C for 2 hours.

Initial mmoles:
p-cyanotoluene 2.56 $BrCCl_3$ 76
p-chlorotoluene 6.91

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-cyanotoluene	2.09	0.47	18.4	0.24
	p-chlorotoluene	2.95	3.96	57.3	
2	*p*-cyanotoluene	2.02	0.54	21.1	0.22
	p-chlorotoluene	2.35	4.56	66.0	
3	*p*-cyanotoluene	2.04	0.52	20.3	0.24
	p-chlorotoluene	2.70	4.21	60.9	
4	*p*-cyanotoluene	1.98	0.58	22.7	0.23
	p-chlorotoluene	2.28	4.63	67.0	

Average $k_{rel} = 0.23 \pm 0.01$

Table 40. Relative rate of disappearance for 3,5-dibromotoluene *vs.* *p*-chlorotoluene in bromotrichloromethane. Photoinitiated at 70°C for 4.0 hours.

Initial mmoles:
3,5-dibromotoluene 0.81 $BrCCl_3$ 25
p-chlorotoluene 2.05

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	3,5-dibromotoluene	0.76	0.05	6.2	0.56
	p-chlorotoluene	1.83	0.22	10.7	
2	3,5-dibromotoluene	0.76	0.05	6.2	0.49
	p-chlorotoluene	1.80	0.25	12.2	
3	3,5-dibromotoluene	0.76	0.05	6.2	0.54
	p-chlorotoluene	1.82	0.23	11.2	
4	3,5-dibromotoluene	0.76	0.05	6.2	0.54
	p-chlorotoluene	1.82	0.23	11.2	
5	3,5-dibromotoluene	0.76	0.05	6.2	0.51
	p-chlorotoluene	1.81	0.24	11.7	

Average $k_{rel} = 0.53 \pm 0.02$

Table 41. Relative rate of disappearance for anisole *vs.* *p*-xylene in bromotrichloromethane. Photoinitiated at 70°C for 2 hours.

Initial mmoles:
anisole 4.48 $BrCCl_3$ 76
p-xylene 4.94

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	anisole	3.51	0.97	21.7	0.28
	p-xylene	0.85	4.09	82.8	
2	anisole	3.40	1.08	24.1	0.32
	p-xylene	0.86	4.08	82.6	
3	anisole	3.47	1.01	22.5	0.29
	p-xylene	0.85	4.09	82.8	
4	anisole	3.67	0.81	18.1	0.27
	p-xylene	1.15	3.79	76.7	
5	anisole	3.69	0.79	17.6	0.40
	p-xylene	1.08	3.07	62.1	

Average $k_{rel} = 0.31 \pm 0.05$

Appendix 3

Kinetic studies of the relative rates for reactions of substituted toluenes with NBS in carbon tetrachloride. Initiated with AIBN at 70°C.

Table 42. Relative rate of disappearance for *p*-methoxytoluene *vs.* *p*-xylene with NBS in carbon tetrachloride. Photoinitiated at 70°C for 10 hours.

Initial mmoles:					
	p-methoxytoluene	4.91	NBS	5.61	
	p-xylene	5.67	CCl_4	72	
run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-methoxytoluene	1.52	3.39	69.0	3.48
	p-xylene	2.89	2.78	49.0	
2	*p*-methoxytoluene	1.26	3.65	74.3	3.86
	p-xylene	2.80	2.87	50.6	
3	*p*-methoxytoluene	1.05	3.86	78.6	4.28
	p-xylene	2.76	2.91	51.3	
4	*p*-methoxytoluene	1.89	3.02	61.5	3.89
	p-xylene	3.47	2.20	38.8	

Average $k_{rel} = 3.88 \pm 0.28$

Table 43. Relative rate of disappearance for *p*-*t*-butyltoluene *vs.* *p*-xylene with NBS in carbon tetrachloride. Photoinitiated at 70°C for 6 hours.

Initial mmoles:

p-*t*-butyltoluene	4.20	NBS	4.50
p-xylene	5.60	CCl_4	72

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-*t*-butyltoluene	3.17	1.03	24.5	1.04
	p-xylene	3.26	2.34	41.8	
2	*p*-*t*-butyltoluene	2.52	1.68	40.0	1.04
	p-xylene	2.10	3.50	62.5	
3	*p*-*t*-butyltoluene	2.61	1.59	37.9	1.03
	p-xylene	2.23	3.37	60.2	
4	*p*-*t*-butyltoluene	2.81	1.39	33.1	1.10
	p-xylene	2.69	2.91	52.0	
5	*p*-*t*-butyltoluene	2.71	1.49	35.5	1.06
	p-xylene	2.45	3.15	56.2	

Average $k_{rel} = 1.05 \pm 0.03$

Table 44. Relative rate of disappearance for *m*-xylene *vs.* *p*-chlorotoluene with NBS in carbon tetrachloride. Photoinitiated at 70°C for 4 hours.

Initial mmoles:

m-xylene	5.12	NBS	4.50
p-chlorotoluene	4.76	CCl_4	72

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*m*-xylene	1.80	3.32	64.8	1.40
	p-chlorotoluene	3.28	1.48	31.1	
2	*m*-xylene	2.17	2.95	57.6	1.74
	p-chlorotoluene	3.72	1.04	21.8	
3	*m*-xylene	1.94	3.18	62.1	1.61
	p-chlorotoluene	3.57	1.24	26.1	
4	*m*-xylene	2.17	2.95	57.6	1.55
	p-chlorotoluene	3.61	1.15	24.2	
5	*m*-xylene	2.28	2.84	55.5	1.66
	p-chlorotoluene	3.73	1.03	21.6	

Average $k_{rel} = 1.58 \pm 0.12$

Table 45. Relative rate of disappearance for *p*-chlorotoluene *vs.* *p*-xylene with NBS in carbon tetrachloride. Photoinitiated at 70°C for 6 hours.

Initial mmoles:

p-chlorotoluene	4.75	NBS	5.61
p-xylene	5.71	CCl_4	72

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-chlorotoluene	3.66	1.09	22.9	0.37
	p-xylene	1.41	4.30	75.3	
2	*p*-chlorotoluene	3.47	1.28	26.9	0.38
	p-xylene	1.10	4.61	80.7	
3	*p*-chlorotoluene	3.26	1.49	31.4	0.46
	p-xylene	1.13	4.58	80.2	
4	*p*-chlorotoluene	3.60	1.15	24.2	0.43
	p-xylene	1.55	4.17	72.9	

Average $k_{rel} = 0.41 \pm 0.04$

Table 46. Relative rate of disappearance for *m*-chlorotoluene *vs.* *p*-xylene with NBS in carbon tetrachloride. Photoinitiated at 70°C for 3 hours.

Initial mmoles:

m-chlorotoluene	4.67	NBS	4.50
p-xylene	5.25	CCl_4	72

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*m*-chlorotoluene	4.32	0.35	7.5	0.10
	p-xylene	1.04	4.21	80.2	
2	*m*-chlorotoluene	4.09	0.58	12.4	0.11
	p-xylene	0.44	4.81	91.6	
3	*m*-chlorotoluene	4.26	0.41	8.8	0.08
	p-xylene	0.59	4.66	88.8	
4	*m*-chlorotoluene	3.76	0.91	19.5	0.13
	p-xylene	0.18	5.07	96.6	
5	*m*-chlorotoluene	4.30	0.37	7.9	0.08
	p-xylene	0.75	4.50	85.7	

Average $k_{rel} = 0.10 \pm 0.02$

Table 47. Relative rate of disappearance for *m*-trifluoromethyltoluene *vs.* *p*-chlorotoluene with NBS in carbon tetrachloride. Photoinitiated at 70°C for 6 hours.

Initial mmoles:

m-CF_3-toluene	0.95	NBS	2.0
p-chlorotoluene	1.61	CCl_4	31

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*m*-CF_3-toluene	0.25	0.70	73.7	0.27
	p-chlorotoluene	0.012	1.598	99.3	
2	*m*-CF_3-toluene	0.62	0.33	34.7	0.19
	p-chlorotoluene	0.18	1.43	88.8	
3	*m*-CF_3-toluene	0.70	0.25	26.3	0.21
	p-chlorotoluene	0.38	1.23	76.4	
4	*m*-CF_3-toluene	0.43	0.52	54.7	0.20
	p-chlorotoluene	0.029	1.581	98.2	
5	*m*-CF_3-toluene	0.36	0.59	62.1	0.20
	p-chlorotoluene	0.012	1.598	99.3	

Average $k_{rel} = 0.21 \pm 0.03$

Table 48. Relative rate of disappearance for *p*-cyanotoluene *vs. p*-chlorotoluene with NBS in carbon tetrachlroide. Photoinitiated at 70°C for 10 hours.

Initial mmoles:					
	p-cyanotoluene	5.21	NBS	5.60	
	p-chlorotoluene	4.80	CCl_4	72	
run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-cyanotoluene	1.56	3.65	70.1	0.35
	p-chlorotoluene	0.15	4.65	96.9	
2	*p*-cyanotoluene	3.16	2.05	39.3	0.27
	p-chlorotoluene	0.74	4.06	84.6	
3	*p*-cyanotoluene	3.58	1.63	31.3	0.32
	p-chlorotoluene	1.49	3.31	69.0	

Average $k_{rel} = 0.31 \pm 0.03$

Table 49. Relative rate of disappearance for 3,5-dibromotoluene *vs.* *p*-chlorotoluene with NBS in carbon tetrachloride. Photoinitiated at 70°C for 8 hours.

Initial mmoles:				
3,5-dibromotoluene	0.82	NBS	2.0	
p-chlorotoluene	1.62	CCl_4	31	

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	3,5-dibromotoluene	0.66	0.16	19.5	0.13
	p-chlorotoluene	0.32	1.30	80.2	
2	3,5-dibromotoluene	0.46	0.36	43.9	0.22
	p-chlorotoluene	0.12	1.50	92.6	
3	3,5-dibromotoluene	0.68	0.14	17.1	0.12
	p-chlorotoluene	0.36	1.26	77.8	
4	3,5-dibromotoluene	0.64	0.18	22.0	0.14
	p-chlorotoluene	0.26	1.36	84.0	
5	3,5-dibromotoluene	0.69	0.13	15.9	0.12
	p-chlorotoluene	0.37	1.25	77.2	

Average $k_{rel} = 0.15 \pm 0.04$

Appendix 4

Kinetic studies of the relative rates for reactions of substituted toluenes with bromotrichloromethane at different concentrations and different temperatures. Photoinitiated.

Table 50. Relative rate of disappearance for *p*-methoxytoluene *vs. p*-xylene in bromotrichloromethane (1:1:10). Photoinitiated at 70°C for 1.75 hours.

Initial mmoles:
p-methoxytoluene 5.01 $BrCCl_3$ 70
p-xylene 4.76

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-methoxytoluene	4.44	0.57	11.4	2.75
	p-xylene	4.36	0.40	8.4	
2	*p*-methoxytoluene	3.56	1.45	28.9	2.18
	p-xylene	3.48	1.28	26.9	
3	*p*-methoxytoluene	3.95	1.06	21.2	2.19
	p-xylene	3.83	0.93	19.5	
4	*p*-methoxytoluene	3.74	1.27	25.3	2.23
	p-xylene	3.66	1.10	23.1	
5	*p*-methoxytoluene	4.52	0.49	9.8	2.62
	p-xylene	4.40	0.36	7.6	
6	*p*-methoxytoluene	3.46	1.55	30.9	2.34
	p-xylene	3.47	1.29	27.1	

Average $k_{rel} = 2.39 \pm 0.24$

Table 51. Relative rate of disappearance for *p*-methoxytoluene *vs.* *p*-xylene in bromotrichloromethane (1:1:4). Photoinitiated at 70°C for 1.5 hours.

Initial mmoles:

p-methoxytoluene	4.71	$BrCCl_3$	18.7
p-xylene	4.76	CH_2Cl_2	75

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-methoxytoluene	3.40	1.31	27.8	2.48
	p-xylene	3.66	1.10	23.1	
2	*p*-methoxytoluene	3.50	1.21	25.7	2.28
	p-xylene	3.67	1.09	22.9	
3	*p*-methoxytoluene	3.51	1.20	25.5	2.31
	p-xylene	3.69	1.07	22.5	
4	*p*-methoxytoluene	3.43	1.28	27.2	2.39
	p-xylene	3.65	1.11	23.3	
5	*p*-methoxytoluene	3.35	1.36	28.9	2.32
	p-xylene	3.55	1.21	25.4	

Average $k_{rel} = 2.36 \pm 0.07$

Table 52. Relative rate of disappearance for *p*-methoxytoluene *vs.* *p*-xylene in bromotrichloromethane (1:1:1). Photoinitiated at 70°C for 2.25 hours.

Initial mmoles:

p-methoxytoluene	4.82	$BrCCl_3$	4.86
p-xylene	4.63	CH_2Cl_2	91

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-methoxytoluene	3.71	1.11	23.0	2.33
	p-xylene	3.70	0.93	20.1	
2	*p*-methoxytoluene	3.66	1.16	24.1	2.24
	p-xylene	3.62	1.01	21.8	
3	*p*-methoxytoluene	3.30	1.52	31.5	2.18
	p-xylene	3.27	1.36	29.4	
4	*p*-methoxytoluene	3.36	1.46	30.3	2.32
	p-xylene	3.39	1.24	26.8	
5	*p*-methoxytoluene	3.41	1.41	29.3	2.28
	p-xylene	3.42	1.21	26.1	
6	*p*-methoxytoluene	4.08	0.74	15.4	2.45
	p-xylene	4.04	0.59	12.7	
7	*p*-methoxytoluene	4.03	0.79	16.4	2.49
	p-xylene	4.01	0.62	13.4	
8	*p*-methoxytoluene	4.09	0.73	15.1	2.60
	p-xylene	4.08	0.55	11.9	

Average $k_{rel} = 2.36 \pm 0.13$

Table 53. Relative rate of disappearance for *p*-methoxytoluene *vs.* *p*-xylene in bromotrichloromethane (1:1:0.5). Photoinitiated at 70°C for 2.25 hours.

Initial mmoles:

p-methoxytoluene	5.08	$BrCCl_3$	2.52
p-xylene	5.09	CH_2Cl_2	75

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-methoxytoluene	4.62	0.46	9.1	2.59
	p-xylene	4.73	0.36	7.1	
2	*p*-methoxytoluene	4.24	0.84	16.5	2.34
	p-xylene	4.36	0.73	14.3	
3	*p*-methoxytoluene	4.46	0.62	12.0	2.47
	p-xylene	4.58	0.51	10.0	
4	*p*-methoxytoluene	4.57	0.51	10.0	2.46
	p-xylene	4.67	0.42	8.3	
5	*p*-methoxytoluene	4.46	0.62	12.2	2.23
	p-xylene	4.53	0.56	11.0	
6	*p*-methoxytoluene	4.49	0.59	11.6	2.25
	p-xylene	4.56	0.53	10.4	

Average $k_{rel} = 2.39 \pm 0.13$

Table 54. Relative rate of disappearance for *p*-methoxytoluene *vs.* *p*-xylene in bromotrichloromethane. Photoinitiated at 60°C for 3 hours.

Initial mmoles:				
p-methoxytoluene	8.51	$BrCCl_3$	156	
p-xylene	9.89			

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-methoxytoluene	1.82	6.69	78.6	2.61
	p-xylene	3.04	6.85	69.3	
2	*p*-methoxytoluene	0.49	8.02	94.2	2.72
	p-xylene	1.21	8.68	87.8	
3	*p*-methoxytoluene	0.82	7.69	90.4	2.66
	p-xylene	1.70	8.19	82.8	
4	*p*-methoxytoluene	0.97	7.54	88.6	2.68
	p-xylene	1.96	7.93	80.2	
5	*p*-methoxytoluene	4.91	3.60	42.3	2.45
	p-xylene	6.31	3.58	36.2	

Average $k_{rel} = 2.62 \pm 0.09$

Table 55. Relative rate of disappearance for *p*-methoxytoluene *vs.* *p*-xylene in bromotrichloromethane. Photoinitiated at 50°C for 3 hours.

Initial mmoles:
p-methoxytoluene 8.51 $BrCCl_3$ 156
p-xylene 9.89

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-methoxytoluene	2.00	6.51	76.5	2.79
	p-xylene	3.50	6.39	64.6	
2	*p*-methoxytoluene	3.45	5.06	59.5	2.77
	p-xylene	5.15	4.74	47.9	
3	*p*-methoxytoluene	1.84	6.67	78.4	2.84
	p-xylene	3.37	6.52	65.9	
4	*p*-methoxytoluene	2.27	6.24	73.3	2.76
	p-xylene	3.79	6.10	61.7	
5	*p*-methoxytoluene	1.73	6.78	79.7	2.82
	p-xylene	3.19	6.70	67.7	

Average $k_{rel} = 2.79 \pm 0.03$

Table 56. Relative rate of disappearance for *p*-methoxytoluene *vs.* *p*-xylene in bromotrichloromethane. Photoinitiated at 40°C for 3 hours.

Initial mmoles:
p-methoxytoluene 8.51 $BrCCl_3$ 156
p-xylene 9.89

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*p*-methoxytoluene	5.18	3.33	39.1	3.11
	p-xylene	7.19	2.70	27.3	
2	*p*-methoxytoluene	6.33	2.18	25.6	2.61
	p-xylene	7.88	2.01	20.3	
3	*p*-methoxytoluene	7.54	0.97	11.4	3.45
	p-xylene	9.22	0.67	6.8	
4	*p*-methoxytoluene	6.72	1.79	21.0	2.64
	p-xylene	8.27	1.62	16.4	

Average $k_{rel} = 2.95 \pm 0.35$

Appendix 5

Kinetic studies of the relative rates for reactions of unsubstituted alkylbenzenes with bromotrichloromethane. Initiated with AIBN at 70°C.

Table 57. Relative rate of disappearance for cumene *vs.* ethylbenzene in bromotrichloromethane. AIBN initiated at 70°C for 48 hours.

Initial mmoles:					
	cumene	5.31	$BrCCl_3$	77	
	ethylbenzene	5.91	AIBN	0.7	
run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	cumene	1.16	4.15	78.2	4.86
	ethylbenzene	3.16	2.75	46.5	
2	cumene	1.07	4.24	79.8	4.44
	ethylbenzene	2.87	3.04	51.4	
3	cumene	1.18	4.13	77.8	4.41
	ethylbenzene	2.99	2.92	49.4	
4	cumene	0.93	4.38	82.5	4.32
	ethylbenzene	2.64	3.27	55.3	

Average $k_{rel} = 4.51 \pm 0.21$

Table 58. Relative rate of disappearance for *sec*-butylbenzene *vs.* ethylbenzene in bromotrichloromethane. AIBN initiated at 70°C for 96 hours.

Initial mmoles:

sec-butylbenzene	4.47	$BrCCl_3$	76
ethylbenzene	5.65	AIBN	1.2

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*sec*-butylbenzene	2.09	2.38	53.2	2.05
	ethylbenzene	2.69	2.96	52.4	
2	*sec*-butylbenzene	1.84	2.63	58.8	2.09
	ethylbenzene	2.42	3.23	57.2	
3	*sec*-butylbenzene	2.08	2.39	53.5	2.06
	ethylbenzene	2.69	2.96	52.4	
4	*sec*-butylbenzene	2.26	2.21	49.4	2.02
	ethylbenzene	2.88	2.77	49.0	
5	*sec*-butylbenzene	2.67	1.80	40.3	1.88
	ethylbenzene	3.27	2.38	42.1	

Average $k_{rel} = 2.02 \pm 0.07$

Table 59. Relative rate of disappearance for 3-phenylpentane *vs.* ethylbenzene in bromotrichloromethane. AIBN initiated at 70°C for 96 hours.

Initial mmoles:

3-phenylpentane	4.06	$BrCCl_3$	76
ethylbenzene	5.65	AIBN	1.3

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	3-phenylpentane	2.47	1.59	39.2	0.55
	ethylbenzene	0.92	4.73	83.7	
2	3-phenylpentane	2.37	1.69	41.6	0.58
	ethylbenzene	0.87	4.78	84.6	
3	3-phenylpentane	2.93	1.13	27.8	0.51
	ethylbenzene	1.57	4.08	72.2	
4	3-phenylpentane	2.41	1.65	40.6	0.58
	ethylbenzene	0.94	4.71	83.4	
5	3-phenylpentane	2.32	1.74	42.9	0.60
	ethylbenzene	0.87	4.78	84.6	
6	3-phenylpentane	2.33	1.73	42.6	0.58
	ethylbenzene	0.84	4.81	85.1	

Average $k_{rel} = 0.57 \pm 0.03$

Table 60. Relative rate of disappearance for *n*-propylbenzene *vs.* ethylbenzene in bromotrichloromethane. AIBN initiated at 70°C for 96 hours.

Initial mmoles:					
	n-propylbenzene	4.33	$BrCCl_3$	76	
	ethylbenzene	5.65	AIBN	1.2	
run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*n*-propylbenzene	2.55	1.78	41.1	0.64
	ethylbenzene	2.47	3.18	56.3	
2	*n*-propylbenzene	2.56	1.77	40.9	0.60
	ethylbenzene	2.37	3.28	58.1	
3	*n*-propylbenzene	2.43	1.90	43.9	0.62
	ethylbenzene	2.24	3.41	60.4	
4	*n*-propylbenzene	2.70	1.63	37.6	0.61
	ethylbenzene	2.60	3.05	54.0	
5	*n*-propylbenzene	2.81	1.52	35.1	0.59
	ethylbenzene	2.70	2.95	52.2	
6	*n*-propylbenzene	2.72	1.61	37.2	0.61
	ethylbenzene	2.62	3.03	53.6	

Average $k_{rel} = 0.61 \pm 0.02$

Table 61. Relative rate of disappearance for *iso*-butylbenzene *vs.* ethylbenzene in bromotrichloromethane. AIBN initiated at 70°C for 96 hours.

Initial mmoles:				
iso-butylbenzene	4.08	$BrCCl_3$	76	
ethylbenzene	5.96	AIBN	1.7	

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*iso*-butylbenzene	3.04	1.04	25.5	0.38
	ethylbenzene	2.73	3.23	54.2	
2	*iso*-butylbenzene	2.60	1.48	36.3	0.45
	ethylbenzene	2.18	3.78	63.4	
3	*iso*-butylbenzene	2.71	1.37	33.6	0.44
	ethylbenzene	2.37	3.59	60.2	
4	*iso*-butylbenzene	2.50	1.58	38.7	0.47
	ethylbenzene	2.10	3.86	64.8	
5	*iso*-butylbenzene	2.79	1.29	31.6	0.44
	ethylbenzene	2.49	3.47	58.2	
6	*iso*-butylbenzene	2.86	1.22	29.9	0.40
	ethylbenzene	2.46	3.50	58.7	

Average $k_{rel} = 0.43 \pm 0.03$

Table 62. Relative rate of disappearance for *neo*-pentylbenzene *vs. iso*-butylbenzene in bromotrichloromethane. AIBN initiated at 70°C for 240 hours.

Initial mmoles:					
	neo-pentylbenzene	1.19	$BrCCl_3$	76	
	iso-butylbenzene	4.51	AIBN	1.6	
run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*neo*-pentylbenzene	1.18	0.01	0.8	0.014
	iso-butylbenzene	2.69	1.82	40.4	

Upper limit of the k_{rel} from 1 run = 0.014

Appendix 6

Kinetic studies of the relative rates for reactions of α- and β-chloroepoxides with triphenyltin hydride. Photoinitiated or AIBN initiated at 70°C.

Table 63. Relative rate of disappearance for *trans*-1-chloro-1,2-epoxypropane *vs.* 2-chloroepoxypropane with triphenyltin hydride. Photoinitiated at 70°C for 5 hours.

Initial mmoles:
trans-1-chloro-1,2-epoxypropane 0.141 Ph_3SnH 0.345
2-chloro-1,2-epoxypropane 0.151

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*trans*-1-chloro...	0.105	0.036	25.5	0.31
	2-chloroepoxyprop..	0.059	0.092	60.9	
2	*trans*-1-chloro...	0.129	0.012	8.5	0.19
	2-chloroepoxyprop..	0.095	0.056	37.1	
3	*trans*-1-chloro...	0.109	0.032	22.7	0.35
	2-chloroepoxyprop..	0.073	0.078	51.7	

Average $k_{rel} = 0.29 \pm 0.07$

Table 64. Relative rate of disappearance for *cis*-1-chloro-1,2-epoxypropane *vs.* 2-chloroepoxypropane with triphenyltin hydride. Photoinitiated at 70°C for 5 hours.

Initial mmoles:
cis-1-chloro-1,2-epoxypropane 0.097 Ph_3SnH 0.345
2-chloro-1,2-epoxypropane 0.151

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*cis*-1-chloroepoxy..	0.070	0.027	27.8	0.35
	2-chloroepoxyprop..	0.059	0.092	60.9	
2	*cis*-1-chloroepoxy..	0.089	0.008	8.2	0.19
	2-chloroepoxyprop..	0.095	0.056	37.1	
3	*cis*-1-chloroepoxy..	0.070	0.027	27.8	0.45
	2-chloroepoxyprop..	0.073	0.078	51.7	

Average $k_{rel} = 0.33 \pm 0.11$

Table 65. Relative rate of disappearance for 2-chloro-1,2-epoxypropane *vs.* neophyl chloride with triphenyltin hydride. Photoinitiated at 70°C for 3.5 hours.

Initial mmoles:
2-chloro-1,2-epoxypropane 0.52 Ph_3SnH 0.72
neophyl chloride 0.50

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	2-chloroepoxyprop..	0.46	0.06	11.5	0.37
	neophyl chloride	0.36	0.14	28.0	
2	2-chloroepoxyprop..	0.44	0.08	15.4	0.27
	neophyl chloride	0.27	0.23	46.0	
3	2-chloroepoxyprop..	0.49	0.03	5.8	0.17
	neophyl chloride	0.35	0.15	30.0	

Average $k_{rel} = 0.27 \pm 0.08$

Table 66. Relative rate of disappearance for epichlorohydrin *vs.* neophyl chloride with triphenyltin hydride. AIBN initiated at 70°C for 14 hours.

Initial mmoles:

epichlorohydrin	0.659	Ph_3SnH	0.58
neophyl chloride	0.723	AIBN	0.06

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	epichlorohydrin	0.264	0.395	59.9	4.28
	neophyl chloride	0.584	0.139	19.2	
2	epichlorohydrin	0.244	0.415	63.0	4.34
	neophyl chloride	0.575	0.148	20.5	
3	epichlorohydrin	0.266	0.393	59.6	4.43
	neophyl chloride	0.589	0.134	18.5	
4	epichlorohydrin	0.258	0.401	60.8	4.57
	neophyl chloride	0.589	0.134	18.5	
5	epichlorohydrin	0.233	0.426	64.6	4.87
	neophyl chloride	0.584	0.139	19.2	

Average $k_{rel} = 4.50 \pm 0.21$

Table 67. Relative rate of disappearance for 2-methoxy-1-chloroethane *vs.* cyclohexyl chloride with triphenyltin hydride. AIBN initiated at 70°C for 24 hours.

Initial mmoles:

methoxychloroethane	0.79	Ph_3SnH	0.80
cylcohexyl chloride	0.450	AIBN	0.06

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	methoxychloroethane	0.32	0.47	59.5	0.39
	cylcohexyl chloride	0.045	0.405	90.0	
2	methoxychloroethane	0.30	0.49	62.0	0.41
	cylcohexyl chloride	0.043	0.407	90.4	
3	methoxychloroethane	0.33	0.46	58.2	0.39
	cylcohexyl chloride	0.047	0.403	89.6	
4	methoxychloroethane	0.30	0.49	62.0	0.43
	cylcohexyl chloride	0.047	0.403	89.6	
5	methoxychloroethane	0.32	0.47	59.5	0.38
	cylcohexyl chloride	0.041	0.409	90.9	
6	methoxychloroethane	0.32	0.47	59.5	0.39
	cylcohexyl chloride	0.045	0.405	90.0	

Average $k_{rel} = 0.40 \pm 0.02$

Table 68. Relative rate of disappearance for epichlorohydrin *vs.* cyclohexyl chloride with triphenyltin hydride. AIBN initiated at 70°C for 14 hours.

Initial mmoles:

epichlorohydrin	0.724	Ph_3SnH	0.63
cylcohexyl chloride	0.860	AIBN	0.04

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	epichlorohydrin	0.395	0.329	45.5	1.97
	cylcohexyl chloride	0.632	0.228	26.5	
2	epichlorohydrin	0.395	0.329	45.5	2.02
	cylcohexyl chloride	0.637	0.223	25.9	
3	epichlorohydrin	0.391	0.333	46.0	2.00
	cylcohexyl chloride	0.632	0.228	26.5	

Average $k_{rel} = 2.00 \pm 0.02$

Table 69. Relative rate of disappearance for *erythro*-3-chloro-1,2-epoxybutane *vs.* cyclohexyl chloride with triphenyltin hydride. AIBN initiated at 70°C for 14 hours.

Initial mmoles:

erythro-3-chloro-1,2-epoxybutane	0.615	Ph_3SnH	0.55
cylcohexyl chloride	0.674	AIBN	0.02

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*erythro* isomer	0.232	0.383	62.3	5.42
	cylcohexyl chloride	0.563	0.111	16.5	
2	*erythro* isomer	0.232	0.383	62.3	5.07
	cylcohexyl chloride	0.556	0.118	17.5	
3	*erythro* isomer	0.226	0.389	63.3	5.20
	cylcohexyl chloride	0.556	0.118	17.5	
4	*erythro* isomer	0.232	0.383	62.3	5.07
	cylcohexyl chloride	0.556	0.118	17.5	

Average $k_{rel} = 5.19 \pm 0.14$

Table 70. Relative rate of disappearance for *threo*-3-chloro-1,2-epoxybutane *vs.* cyclohexyl chloride with triphenyltin hydride. AIBN initiated at 70°C for 10 hours.

Initial mmoles:
threo-3-chloro-1,2-epoxybutane 0.626 Ph_3SnH 0.64
cylcohexyl chloride 0.599 AIBN 0.03

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*threo* isomer	0.133	0.493	78.8	5.82
	cylcohexyl chloride	0.459	0.140	23.4	
2	*threo* isomer	0.133	0.493	78.8	5.82
	cylcohexyl chloride	0.459	0.140	23.4	
3	*threo* isomer	0.133	0.493	78.8	6.01
	cylcohexyl chloride	0.463	0.136	22.7	
4	*threo* isomer	0.153	0.473	75.6	5.47
	cylcohexyl chloride	0.463	0.136	22.7	

Average $k_{rel} = 5.78 \pm 0.20$

Table 71. Relative rate of disappearance for *trans*-2-chloro-7-oxabicycloheptane *vs*. cyclohexyl chloride with triphenyltin hydride. AIBN initiated at 70°C for 10 hours.

Initial mmoles:
trans-2-chloro-7-oxabicyclo [4.1.0] heptane 0.704 Ph_3SnH 0.70
cylcohexyl chloride 0.683 AIBN 0.08

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*trans* isomer	0.272	0.432	61.4	5.06
	cylcohexyl chloride	0.566	0.117	17.1	
2	*trans* isomer	0.255	0.449	63.8	5.21
	cylcohexyl chloride	0.562	0.121	17.7	
3	*trans* isomer	0.238	0.466	66.2	5.77
	cylcohexyl chloride	0.566	0.117	17.1	
4	*trans* isomer	0.233	0.471	66.9	5.67
	cylcohexyl chloride	0.562	0.121	17.7	
5	*trans* isomer	0.227	0.477	67.8	5.60
	cylcohexyl chloride	0.558	0.125	18.3	

Average $k_{rel} = 5.46 \pm 0.28$

Table 72. Relative rate of disappearance for *cis*-2-chloro-7-oxabicycloheptane *vs*. cyclohexyl chloride with triphenyltin hydride. AIBN initiated at 70°C for 8 hours.

Initial mmoles:

cis-2-chloro-7-oxabicyclo [4.1.0] heptane	0.256	Ph_3SnH	0.25
cylcohexyl chloride	0.253	AIBN	0.02

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	*cis* isomer	0.057	0.199	77.7	11.11
	cylcohexyl chloride	0.221	0.032	12.6	
2	*cis* isomer	0.057	0.199	77.7	9.79
	cylcohexyl chloride	0.217	0.036	14.2	
3	*cis* isomer	0.049	0.207	80.9	12.23
	cylcohexyl chloride	0.221	0.032	12.6	

Average $k_{rel} = 11.04 \pm 1.00$

Table 73. Relative rate of disappearance for benzyl chloride *vs.* cyclohexyl chloride with triphenyltin hydride. AIBN initiated at 70°C for 8 hours.

Initial mmoles:

benzyl chloride	0.935	Ph_3SnH	0.59
cylcohexyl chloride	0.818	AIBN	0.04

run #	Compound	mmoles final	mmoles used	percent reacted	k_{rel}
1	benzyl chloride	0.45	0.485	51.9	21.79
	cylcohexyl chloride	0.791	0.027	3.3	
2	benzyl chloride	0.45	0.485	51.9	21.00
	cylcohexyl chloride	0.790	0.028	3.4	
3	benzyl chloride	0.45	0.485	51.9	24.56
	cylcohexyl chloride	0.794	0.024	2.9	

Average $k_{rel} = 22.45 \pm 1.53$