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THE REACTIONS OF ATOMIC HYDROGEN IN SOLUTION

BY

LIYING ZHANG ©

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1994

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TO MY PARENTS,

MY HUSBAND AND MY SON

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To my family.

ABSTRACT

The solution phase reactions of atomic hydrogen with olefins have been studied at low temperature. Hydrogen or deuterium atoms produced from hydrogen or molecular deuterium in the cavity of a microwave generator were allowed to react with two olefins: 1-octene and 1-methylcyclohexene. A detailed mechanism for the formation of the products, both monomers and dimers, was determined. The addition reactions were regioselective, >99% addition to the terminal carbon of 1-octene and >99% to the secondary carbon of 1-methylcyclohexene. No products from allylic abstraction were detected. The disproportionation to combination ratios (k_d/k_c) of the 1-methylheptyl and 1-methylcyclohexyl radicals were determined at different temperatures. The extrapolated ratios were found to be in good agreement with the literature values reported for reactions studied at room temperature.

The 1-methyl-5-hexenyl radical formed by the addition of a hydrogen atom to the terminal position of 1,6-heptadiene led to a complex mixture of products resulting from open chain and cyclized radicals. The cyclized radicals were formed reversibly and the final product mixture contained only minor amounts of *cis*-1,2-dimethylcyclopentane (the product of kinetic control) while the major cyclized product was methylcyclohexane. Although an equilibrium mixture could not be obtained the dimethylcyclopentyl and 3-methylcyclohexyl radicals were shown to be formed reversibly.

The hydrogenations of 1-methylcyclohexene and 1-octene were both carried out in the presence of carbon tetrachloride or bromotrichloromethane. Along with the expected products, 7,7-dichloro-1-methylbicyclo[4.1.0]-heptane and 1,1-dichloro-2-hexylcyclopropane were formed. The formation

of the bicyclic product was shown to be the result of a radical displacement on carbon. The rate constants for the cyclization were estimated using competition kinetics.

The reactions of hydrogen atoms with a series of unsymmetric disulfides were carried out. The regioselectivities and mechanisms of the reactions were investigated. The primary products of the reactions are thiol and thiyl radicals. The symmetric disulfides in the product mixtures were formed at −78 °C by radical combination reactions, and not by radical displacements on the unsymmetric disulfides. The reactions of hydrogen atoms with a series of unsymmetric sulfides were carried out. A mechanism was proposed in which atomic hydrogen adds to the sulfur and forms an intermediate. The cleavage of the intermediate favors the most stable radical.

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ABBREVIATIONS

The following abbreviations are used throughout the thesis:

APT	attached proton test
δ	NMR chemical shift
DMSO	dimethyl sulfoxide, CH_3SOCH_3, a solvent
EPR	electron paramagnetic resonance
eq.	equation
Et	ethyl
Fig.	figure
GC	gas phase chromatography
h	hour
HPLC	high pressure liquid chromatography
IR	infrared spectroscopy
m	*meta*
Me	methyl
MS	mass spectroscopy
min.	minutes
NMR	nuclear magnetic resonance
o	*ortho*
p	*para*
Ph	phenyl
r.t	room temperature
ν	wave number

CHAPTER 1

The Reactions of Atomic Hydrogen in the Vapor and Solution Phases

1. A Brief History of Hydrogen Atom Production

Since the first report of the dissociation of molecular hydrogen on hot tungsten filaments in 1911,[1] many methods have been developed for the generation of hydrogen atoms. The most frequently used method is the so-called Wood's tube,[2] in which a low-pressure stream of molecular hydrogen passes over metallic electrodes held at a relatively high voltage. Other common methods include: (1) radiofrequency and high-frequency microwave discharges, (2) mercury-photosensitized decomposition of H_2 and hydrocarbons, (3) direct photolysis of several compounds, (4) radiolysis of paraffins, (5) certain flame reactions, and (6) shock tube reactions.

Jennings and Linnett[3] first described an efficient way of producing high concentrations of hydrogen atoms in 1958. They were able to maintain the discharge with 350 W of 9.7 MHz radiation and a gas pressure of about 0.08 torr. This gave about 50-60% dissociation of H_2 into H atoms. The development of powerful sources of microwave energy during World War II resulted in the widespread use of microwave discharges for the dissociation of gases. Nagle, *et al.*,[4] and Broida and Moyer,[5] found that a microwave discharge provides an efficient, stable source of hydrogen atoms. The microwave source has the advantage of having the energy readily and efficiently coupled to the H_2 gas discharge. The mercury (Hg $^3P_1$) photosensitized decomposition of H_2 has proven to be a convenient source of hydrogen atoms.[6-8] Hydrogen atoms may also be produced by the mercury (Hg $^3P_1$) photosensitized decomposition of hydrocarbons.[9-12] The direct photolysis of many compounds, e.g., HBr,[13-14] HI,[15-16] HCHO,[17] thiols,[18,22-23] H_2S,[19-20] and *tert*-butyl peroxyformate[24] results in the production of hot ground state ($^2S_{1/2}$) hydrogen atoms. These hot atoms have excessive translation energy (from 22 to 40 kcal/mol) depending on the wavelength of the photolysis source. In an excess of inert gas, or in the liquid phase, these hot atoms will be deactivated rapidly by collisions and react as thermalized atoms.[21] Hydrogen atoms may also be produced by radiolysis. Yang[25] produced H atoms by γ radiolysis of propane, and Back[26] has used α radiolysis of hydrocarbons to produce H atoms. Hardwick[27] produced H atoms by X-ray radiolysis of alkane solvents. These techniques have been used primarily for measurements of competitive reactions, yielding ratios of the rate constants of competing reactions. Hydrogen atoms are present during the combustion of mixtures of H_2, H_2-O_2, H_2-CO, and hydrocarbons.[28-29] The thermal dissociation of hydrogen behind a shock wave was described by Gardiner and Kistiakowsky.[30]

2. Addition of atomic hydrogen to olefins in the gas phase

When atomic hydrogen reacts with olefinic hydrocarbons, excited alkyl radicals are formed. The subsequent unimolecular dissociation of these radicals has been the subject of extensive experimental and theoretical studies.[31]

2.1. Addition to ethylene

The kinetics and mechanism of the reaction of hydrogen atoms with ethylene have been extensively studied. It is generally agreed that the first step in this reaction is the addition of the H atom to form an ethyl radical. The ethyl radical formed would be highly vibrationally excited and could contain up to 39.6 kcal mol^{-1} of excess energy.[31] This radical may do one of two things: (1) it may decompose into the initial materials, (2) it may be deactivated by collisions with the resulting stabilized radical undergoing further reaction. The mechanism is reported as:[31]

$$H\bullet + C_2H_4 \rightleftharpoons C_2H_5\bullet^{*} \longrightarrow C_2H_5\bullet \tag{1}$$

$$H\bullet + C_2H_5\bullet \rightleftharpoons C_2H_6^{**} \longrightarrow 2CH_3\bullet \tag{2}$$

$$H\bullet + CH_3\bullet \rightleftharpoons CH_4^{*} \xrightarrow{M} CH_4 \tag{3}$$

$$CH_3\bullet + CH_3\bullet \rightleftharpoons C_2H_6^{*} \xrightarrow{M} C_2H_6 \tag{4}$$

$$CH_3\bullet + C_2H_5\bullet \longrightarrow C_3H_8 \tag{5}$$

$$C_2H_5\bullet + C_2H_5\bullet \longrightarrow n\text{-}C_4H_{10} \tag{6}$$

The rate constant, determined by various workers for reaction (1) ranges from 0.88×10^{11} cc mol^{-1} sec^{-1} to 8.19×10^{11} cc mol^{-1} sec^{-1}. The activation energy has been determined. It ranges from 0.5 to 3.3 kcal/mol.[32] The value $E = 3.18$ kcal/mol was calculated by Baldwin, *et al.*,[33] based on a combination of the results Yang[25] and Jennings and Cvetanovic.[9]

2.2. Addition to high carbon olefins

The addition of an H atom to an olefin in the vapor phase results in the formation of a vibrationally excited alkyl radical. The excited radical can dissociate, forming either the original H atom and the olefin again or a new radical and olefin. It may also undergo collisional stabilization. The reaction of H atoms with olefins can be described by reactions (7) to (9). The alkyl

$$H\cdot + (\text{olefin})_I \rightleftharpoons R_1\cdot^{*} \qquad (7)$$

$$R_1\cdot^{*} \begin{cases} \longrightarrow R_2\cdot + (\text{olefin})_{II} \\ \xrightarrow{M} R_1\cdot \end{cases} \qquad (8)$$

$$H\cdot + (\text{olefin})_I \longrightarrow H_2 + R_2\cdot \qquad (9)$$

radicals produced in the reaction undergo a termination reaction. The paths available to a pair of radicals are combination, eq 10, and disproportionation, eq 11. Both processes are highly exothermic ($\Delta H^o = -50$ to -95 kcal/mol).

$$RCH_2CH_2\cdot + RCH_2CH_2\cdot \begin{cases} \xrightarrow{k_c} RCH_2CH_2CH_2CH_2R & (10) \\ \xrightarrow[k_d]{} RCH_2CH_3 + RCH{=}CH & (11) \end{cases}$$

$$R_1\cdot + R_2\cdot \begin{cases} \xrightarrow{k_c} R_1\text{-}R_2 \\ \xrightarrow[k_d]{} R_1H + R_2(\text{-}H) \end{cases} \qquad (12)$$

The values k_d/k_c for pairs of the same radicals in the gas phase were reported.[34,35] The value 0.14 for ethyl, propyl, *n*-butyl, and *n*-pentyl radicals was generally agreed upon. For *sec*-butyl radicals, the best value seems to be about 0.7. The ratio of the rate constant, $k_d/k_c = 2.3$ was obtained for *tert*-butyl radicals generated from the photolysis of azo compounds and by hydrogen atom addition to isobutene.

The position of the addition of the hydrogen atom to an olefin in the gas phase has been studied. Hydrogen atoms add predominantly to the less substituted carbon atom of the double bond, in agreement with the behavior of most other atoms and radicals. Moore,[36] Moore and Wall,[37] and Boddy and Robb[38] found exclusively terminal addition of the H atom to propene and 1-butene. Bradley *et al.*,[39] however, had earlier reported 7.5% nonterminal addition of the H atom to propene. The nonterminal addition was based on the ratio of two dimeric products, 2-methylpentane/2,3-dimethylbutane. They ascribed the formation of 2-methylpentane to the combination product of *n*-propyl and *sec*-propyl radicals.

3. The reactions of atomic hydrogen in solution

Reactions in solution have been carried out in aqueous and nonaqueous media. The reactivity of hydrogen atoms in aqueous solutions has been studied extensively.[40] Hydrogen atoms are formed directly by radiolysis of water.

$$H_2O \rightarrow H, e_{aq}^-, OH, H_2, H_2O_2, H^+ \qquad (13)$$

Table I-1 Rate Constants for the Reactions of Hydrogen Atoms with Organic Compounds in Aqueous Solutions[a,b]

Compound	Rate constant M^{-1} sec^{-1}
Acetaldehyde	3.4×10^{7}
Acetamide	1.3×10^{5}
Acetanilide	1.1×10^{9}
Acetate (pH 7)	4.2×10^{5}
Acetic acid	8.4×10^{4}
Acetone	2.8×10^{6}
Acetonitrile	1.5×10^{6}
Acetophenone	1.2×10^{9}
N-Acetylalanine	8.0×10^{6}
N-Acetylglycine	3.8×10^{6}
Acetylenedicarboxylic acid	1.0×10^{9}
Adenine	8.3×10^{7}
Adenosine	1.1×10^{8}
α-Alanine	2.9×10^{5}
β-Alanine	3.4×10^{5}
Aminoacetonitrile	6.6×10^{6}
2-Aminoethanol	3.0×10^{6}
α-Aminoisobutyric acid	8.0×10^{4}
Aniline	4.9×10^{8}
Anisole	1.2×10^{9}
Arbinose	5.7×10^{7}
Arginine	4.9×10^{6}
Ascorbate (pH 7)	$3\text{-}6 \times 10^{8}$
Ascorbic acid	1.1×10^{8}
Asparagine	4.7×10^{5}
Aspartate (pH 7)	2.9×10^{6}
Aspartic acid	8.0×10^{5}
Barbiturate (ph 7)	2.0×10^{9}
Barbituric acid	2.0×10^{7}
Benzaldehyde	1.5×10^{9}
Benzamide	8.9×10^{8}
1,3,5-Benzenetricarboxylic acid	6.5×10^{8}
Benzoate (pH 7)	9.2×10^{8}
Benzoic acid	8.5×10^{8}
Benzonitrile	6.4×10^{8}
Benzyl alcohol	1.1×10^{9}
Betaine	8.0×10^{4}
Bromoacetic acid	2.6×10^{8}
5-Bromoorrotic acid	2.1×10^{8}
5-Bromouracil	2.2×10^{8}
Butane	3.9×10^{7}
Butyl alcohol	3.8×10^{7}
sec-Butyl alcohol	1.3×10^{7}
tert-Butyl alcohol	8.0×10^{4}
Bytyric acid	8.6×10^{6}
Carbon tetrachloride	4.8×10^{7}
Chloroform	1.2×10^{7}
Chlorotrifloromethane	$< 10^{6}$
5-Chlorouracil	1.6×10^{8}
Citric acid	4.3×10^{5}
Cyanoacetic acid	3.2×10^{6}
Cyclohexane	3×10^{7}
Cyclopentane	3×10^{7}
Cyclopropane	7×10^{5}
Cysteine	4×10^{9}
Cyctine	8×10^{9}
Cytosine	9×10^{7}
Dichlorodofluoromethane	$< 10^{6}$
Dichloromethane	4×10^{6}
o-Dicyanobenzene	5.5×10^{8}
m-Dicyanobenzene	5.2×10^{8}
p-Dicyanobenzene	2.8×10^{8}
Diethyl ether	4.7×10^{7}
2,3-Dihydroxyfumaric acid	9×10^{7}
Dioxane	1.3×10^{7}
Dithiodiglycolic acid	1.0×10^{10}
Ethane	2.5×10^{6}
Ethyl alcohol (pH 1, pH 7)	2.6×10^{7}
Ethyl bromide	1.7×10^{8}
Ethyl chloride	1.8×10^{6}
Ethylene	3×10^{9}
Ethylenediaminetetraacetic acid	6.5×10^{7}
Ethylene glycol	1.7×10^{7}
5-Flurouracil	1.8×10^{8}
Formate (pH 7)	1.3×10^{8}
Formic acid	7.4×10^{5}
Fumaric acid	9×10^{8}
Glucose	4.7×10^{7}
Glutamate (pH 7)	5.6×10^{6}
Glutamic acid	1.7×10^{6}
Glycerol	3.6×10^{7}
Glycine	8×10^{4}
Glycolate (pH 7)	4.0×10^{7}
Glycolic acid	1.8×10^{7}
Glycylglycine	2.6×10^{6}
Glycylglycylglycine	5.5×10^{6}
Guanidine	1.3×10^{6}
Hexamethylenimine	1.5×10^{7}
Hexane	1.5×10^{8}
1,6-Hexanediamine	4.7×10^{6}
Hexanoate (pH 7)	5.3×10^{7}
Hexanoic acid	4.6×10^{7}
Hexyl alcohol	1.0×10^{8}
Hexylamine	3.5×10^{7}
Hippuric acid	1.0×10^{9}
Histidine	4.8×10^{7}
4-Hydroxyproline	6.0×10^{6}
Imidazole	6.2×10^{7}
Iminodiacetic acid	4.0×10^{5}
Isobutane	1.2×10^{8}
Isobutyl alcohol	6.4×10^{7}
Isobutyrate (pH 7)	5.9×10^{7}
Isobutyric acid	2.6×10^{7}
Isobutyronitrile	2.2×10^{7}

Compound	Rate constant M^{-1} sec^{-1}	Compound	Rate constant M^{-1} sec^{-1}
Isoleucine	8×10^6	Propionitrile	1.1×10^7
Isoorotic acid	9×10^7	Propyl alcohol	2.5×10^7
Isopropyl alcohol	6.5×10^7	Purine	1.2×10^8
Lactic acid	2.2×10^7	Pyrazine	3.3×10^8
Leucine	1.7×10^7	Pyridazine	2.9×10^8
Lysine	1.6×10^6	Pyridine	2.2×10^8
Maleic acid	6×10^8	Pyrimidine	1.0×10^8
Malic acid	2.2×10^7	Ribose	5.5×10^7
Malonic acid	4.2×10^5	Srcosine	1.2×10^5
Methane	$< 10^5$	Serine	1.3×10^6
Methanol	1.6×10^6	Succinate (pH 7)	1.1×10^7
Methyl chloride	7×10^4	Succinic acid	3.5×10^6
Methyl iodide	$\geq 2 \times 10^9$	Tartaric acid	1.7×10^7
6-Methyluracil	7×10^8	Tartronic acid	2.3×10^7
Neopentyl alcohol	2.9×10^7	Tetrahydrofuran	7.8×10^7
Nitriotriacetic acid	7.5×10^6	*N,N,N',N'*-Tetramethyl-*p*-Phenylenediamine	2.4×10^8
Nitromethane	4.4×10^7		
Orotic acid	5×10^8	Thioacetamide	6×10^9
Oxalate (pH 7)	$\leq 4 \times 10^4$	Thiodiglycolic acid	2×10^9
Oxalic acid	4.1×10^5	Thioglycolic acid	4×10^9
Pentane	7×10^7	Thiomalic acid	3×10^9
Phenol	1.4×10^9	Thiourea	6×10^9
Phenyl acetate	8.6×10^8	Threonine	8×10^6
Phenylacetic acid	9.6×10^8	Thymine	5×10^8
Phenylalanine	8.0×10^8	Trichlorofluoromethane	1.7×10^6
o-Phenylenediamine	7.3×10^8	Trimethylanilinium	4.5×10^8
m-Phenylenediamine	3.4×10^8	Tryptophan	$\geq 2.3 \times 10^9$
p-Phenylenediamine	3.0×10^8	Tyrosine	1.1×10^9
Proline	8×10^5	Uracil	2.8×10^8
Propane	2.2×10^7	Urea	$\leq 3 \times 10^7$
Propionate (pH 7)	1.8×10^7	Valine	9×10^6
Propionic acid	6.4×10^6	Valine (pH 7)	1.3×10^7

[a] Determined by the EPR technique. Solutions at pH 1 unless otherwise stated. [b] Neta, P. *Chem. Rev.* **1972**, *72*, 533.

Reaction mechanisms or rate constants were studied by spectroscopic observation of the intermediate radicals. When stable products have been determined, these were usually H_2, HD,[22-24] or halide ion.[41] Prior to 1960-1962, it was not recognized that both the electron and the hydrogen atom are products of aqueous radiolysis, and consequently the kinetic data which were collected and ascribed to the action of the hydrogen atom alone were in error.[23] The development of the pulse radiolysis technique enabled the measurement of absolute rate constants for the reactions of hydrogen atoms by the spectrophotometric observation of radicals. The kinetic measurements of reactions of the hydrogen atom were acheived by directly observing the EPR signals of the H atom resulting from *in situ* radiolysis. Representative rate constants for the reactions of the hydrogen atoms with an organic compound in an aqueous solution are given in Table I-1.[40] Although extensive kinetic studies have been performed, little study of the organic end products of the reactions of hydrogen atoms has been done.

The reactions of hydrogen atoms in non-aqueous solution have received little attention. A method was described by Hardwick[42] in which hydrogen atoms, produced *in situ* by the radiolysis of a saturated hydrocarbon, were allowed to react competitively with a reactive solute. A kinetic expression was derived whereby the relative rate constants for the competing reactions can be calculated from the measurement of the hydrogen gas as a function of solute concentration. The rates of reaction of hydrogen atoms with a series of olefins in hexane solution were reported as $4.9 - 11.7 \times 10^{11}$ cc $mole^{-1}$ sec^{-1},[43] for olefins with a structural type RCH=CHR, at 23 °C. Absolute rate constants for the reactions of H atoms with paraffins were obtained, and the reaction rate constants for abstraction of primary, secondary and tertiary hydrogen (0.25, 1.10, 7.75×10^6

M^{-1} sec^{-1} respectively, a ratio of 1 : 6.6 : 93) were assigned. In aqueous solution, Neta and Schuler[43] reported that the partial reactivities of CH_3, CH_2, and CH are 0.1, 1, and 2 × 10^7 M^{-1} sec^{-1}. These values yield a ratio of 1 : 15 : 60 for the relative reactivities of primary, secondary, and tertiary hydrogen.

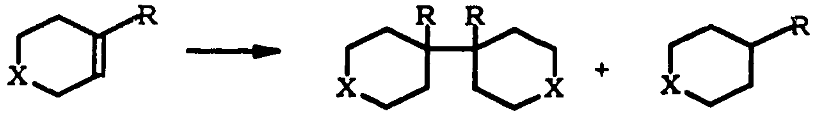
Pryor[23] reported a method for studying the reactions of hydrogen atoms in non-aqueous solutions. Hydrogen atoms, produced by the photolysis of thiols, react with organic hydrogen donors: $QH + H\bullet \rightarrow Q\bullet + H_2$ (k_H) to produce hydrogen gas. The technique used to obtain values of k_H involves measuring the HD/D_2 ratio produced as the solvent (QH) to deuterated thiol ratio is varied. Relative reactivities, per hydrogen, of primary, secondary, and tertiary hydrogens were reported as 1 : 5 : 40 at 35 °C.

Mazur[44] reported the solution phase reaction of hydrogen atoms generated in a microwave discharge with several olefins. Phenyl- and alkylethylenes were converted almost quantitatively into their respective dimers and hydrogenated products, eq 14-16.

$$\underset{1}{\phi CR = CH_2} \rightarrow \underset{3}{\phi C(R)(CH_3)C(R)(CH_3)\phi} + \underset{4}{\phi CHRCH_3} \qquad (14)$$

a R = H
b R = CH_3
c R = ϕ

$$\underset{2}{\phi CR = CHCH_3} \rightarrow \underset{5}{\phi CH(C_2H_5)CH(C_2H_5)\phi} + \underset{6}{\phi (CH_2)_2CH_3} \qquad (15)$$



7 8 9

(16)

	R	X
a	ϕ	CH_2
b	H	CH_2
c	H	$(CH_2)_3$
d	H	$CH_2CH{=}CH_2$
e	CH_3	CH_2

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CHAPTER 2

The Regioselective Addition of Atomic Hydrogen to Olefins. Reversible 1-Methyl-5-hexenyl Radical Cyclization in the Solution Phase Hydrogenation.

*. A version of this chapter has been submitted for publication.
Tanner, D. D.; Zhang, L.Y. *J. Am. Chem. Soc.* **1994,** *116*, 0000 (in press).

Introduction

The rates of addition of atomic hydrogen to olefins in the vapor phase have been reported.[1-16] Although a structure-reactitvity relationship is apparent, secondary processes from vibrationally excited intermediates, (*i.e.*, fragmentation and rearrangement) make an interpretation of these results equivocal.[17-21] Since the reaction rates and products are dependent upon experimental conditions (*e.g.*, pressure, concentration and substrate structures, *etc.*), analysis of a structure-reactivity relationship is by necessity indirect and difficult to interpret. Competition from allylic abstraction is estimated to account for less than 10% of the total reaction products.[1,10-11,22-26] The regioselectivity of these additions reflects the energetics of the reaction, and by using an indirect kinetic analysis the authors are able to report a high selectivity for addition to the terminal end of several olefins (93-99%).[27-33]

Solution phase addition of hydrogen atoms to olefins has been achieved using pulsed radiolysis. The hydrogen atoms generated by the radiolysis of alkane solvents were scavenged using added olefins. In this manner, the relative rates of addition of hydrogen atoms to a variety of olefins were determined.[34] In a preliminary report on the addition of hydrogen atoms generated by microwave discharge to a number of olefins,[35] Mazur established that a mixture of both saturated and dimeric products could be formed in high yield from the reaction of atomic hydrogen with phenyl- or alkyl substituted ethylenes.

Results and Discussion

Using the procedure reported by Mazur[35] hydrogen atoms generated in a microwave discharge were passed over a stirred solution of the reactive substrate. The products formed in these highly chemospecific reactions were analyzed, and the solution phase structure reactivity relationships for the reactions of atomic hydrogen were obtained.

1. Regioselective addition to 1-octene

When atomic hydrogen (0.7-4.4 mmol) is passed over neat 1-octene (–78 °C) the products of the reaction are: octane, *cis*- and *trans*-2-octene, and two structurally different dimeric products (*meso*- and *d,l*-7,8-dimethyltetra-decane and 7-methylpentadecane), see Table II-1.

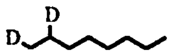
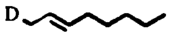
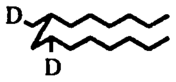
Some insight is obtained concerning the mechanism of the formation of these products by carrying out the reduction with deuterium atoms (–78 °C). The distribution of the products from these reactions are listed in Table II-2. By comparing the mass, ^1H and ^2H NMR of the protiated to those of the deuterated products of the reaction mixture, it is obvious that in each of the products, monomer or dimer, at least one deuterium is attached to a terminal position attributable to the original olefin, see Table II-2. The mass spectra of the products shows 1-octene (d_0 and d_1, A), octane (d_1, B and d_2, C), *trans*-2-octene (d_1, D), *cis*-2-octene (d_1, E), 7,8-dimethyltetradecane (d_2, F), and 7-methylpentadecane (d_2, G). If the assumption is correct that the initial reaction is regiospecific addition to the terminal position of 1-octene, then the deuterated products are those listed

Table II-1. The Product Distribution From the Addition of Atomic Hydrogen to 1-Octene (–78 °C)[a]

Reaction %	H• (mmol)[a]	 [b]		 [b]			 [c]		Reaction Time (min.)
1.1	0.7	20.7	18.0	33.8	10.4	2.6	13.3	1.2	4
2.1	1.3	20.3	20.5	32.8	10.1	2.4	12.9	1.0	7
3.1	2.0	16.4	27.7	29.8	10.9	2.5	11.7	0.9	11
7.1	4.4	12.8	28.6	30.7	13.1	2.8	11.3	1.2	25

[a] Neat 1-octene was used. H_2 flow rate 4 mL/min. The products are listed in mol%.
[b] Calculated using the data from Table II-2. Products formed by the disproportionation reaction.
[c] A (1:1) mixture of *meso*- and *d,l*-dimers.

Table II-2. The Product Distribution from the Addition of Deuterium Atoms to 1-Octene[a,b]

Reaction Time %	(min)	[Olefin]	 A	 B	 C	 D	 E	[c] F	 G	ρ_{MDA}/ρ_{MDE}	k_d/k_c
4.4[d]	20	6.4	17.1	30.8	26.9	9.1	2.8	11.8	1.4	1.06	2.61
8.1[d]	10	1.1	22.3	34.9	14.2	11.0	2.3	14.5	0.9	0.91	2.56
18.8[d]	10	0.7	23.8	34.3	13.0	11.3	2.5	13.4	1.7	0.91	2.56
35.6[d]	90	6.4	16.8	32.6	23.2	11.2	2.4	12.7	1.2	1.07	2.57
3.7[e]	20	6.4	13.6	28.4	24.8	11.5	3.3	16.9	1.5	1.00	1.68
4.2[f]	20	6.4	22.0	34.6	19.4	11.6	2.4	9.3	0.6	0.96	3.72

[a] Concentrations (23 °C) were neat (6.38 M) 1-octene or in acetone. H_2 flow rate 4 ml/min. The products are listed in mol %.

[b] The product distribution was calculated using the data obtained from GC and ^2H NMR analysis.

[c] A (1:1) mixture of *meso*- and *d,l*-dimers.

[d] Reactions were carried out at -78 °C.

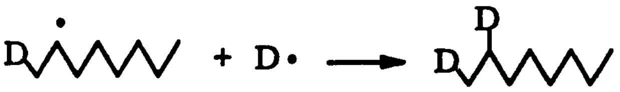
[e] Reaction was carried out at -42° C.

[f] Reaction was carried out at -100 °C.

in Table II-2. The ^2H NMR show absorption with intensity (I_n) at δ 1.00 (DCH_2-, I_1), 1.40 (-CDH-, I_2), 1.65 (DCH_2-CH=C-, I_3), and 5.10 (DCH=CH-, I_4), see Fig. II-1. From the concentrations of the products, the distribution of the deuterated products is calculated, see Table II-2. The proportionality constant, f, is obtained from the equation, $I_3 = ([D] + [E])/f$, and the unknown product concentrations are obtained using the following relationships; $[A] = fI_4$; $[C] = (fI_2-[G]/f$; $[B] = fI_1-fI_2-2[F]$. The first step in the hydrogenation is no doubt addition to the terminal position of the olefin (eq 1).

(1)

When the secondary radical encounters deuterium atom, 1,2-dideuteriooctane is formed (eq 2), see Appendix II-1A.



(2)

The major saturated or unsaturated hydrocarbon, however, contains only one deuterium atom. The incorporation of protium into octene can be attributed to disproportionation (eq 3).

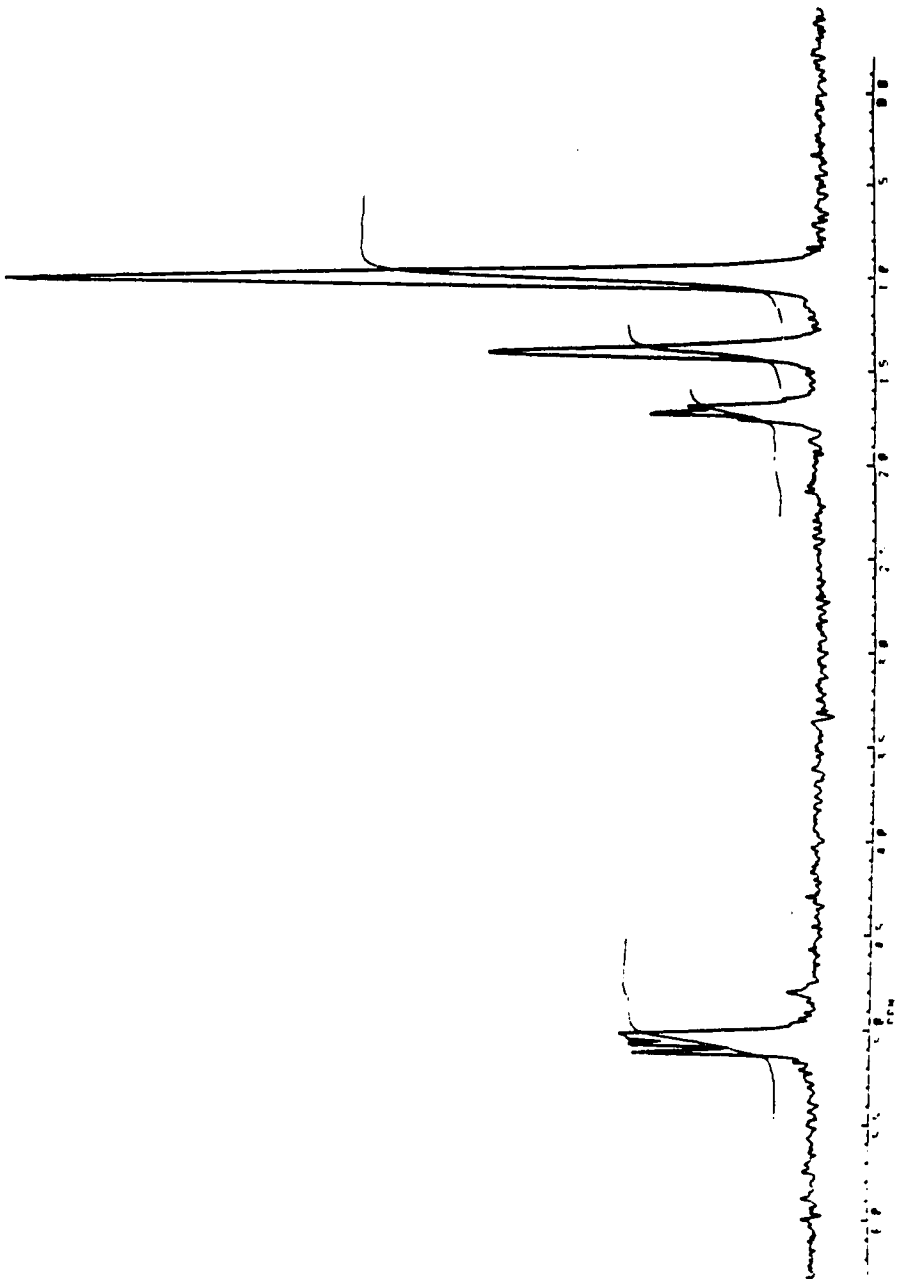
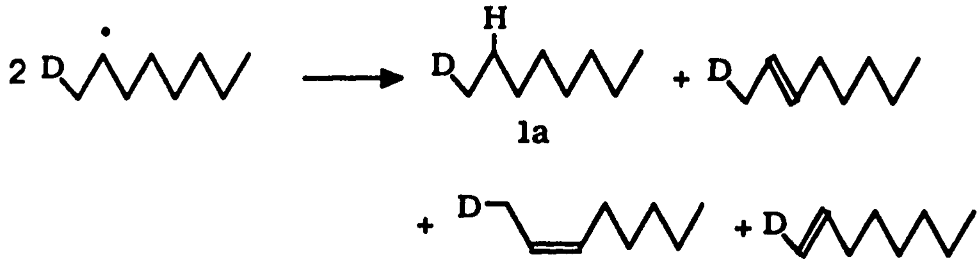
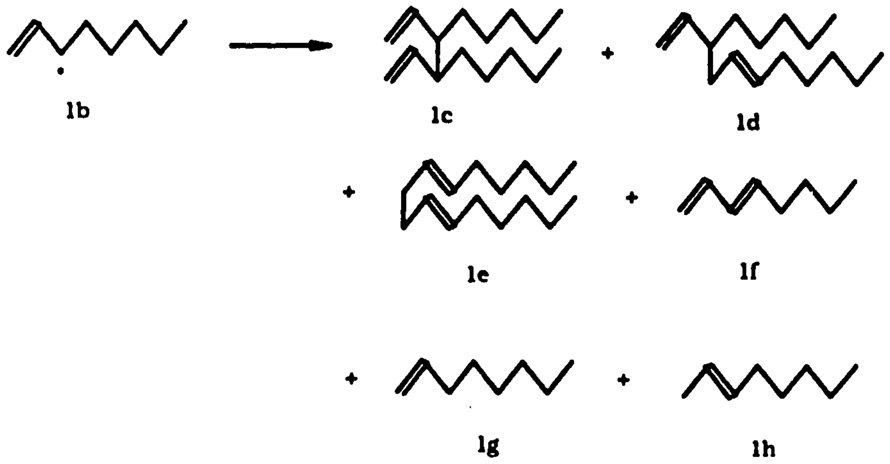


Fig. II-1. The ^{2}H NMR spectrum of the reaction product mixture of deuterium atoms addition to 1-octene.


1a

(3)

The observation that the ratio of monodeuterated octane to octenes, (ρ_{MDA} / ρ_{MDE}) equals 1.00, is consistent with the disproportionation pathway (eq 3). During the treatment of 1-octene with deuterium a monodeuterated alkene can conceivably arise via allylic abstraction followed by reaction with a deuterium atom, however the 1:1 ratio, ρ_{MDA}/ρ_{MDE}, makes this possibility unattractive. The observation that allylic abstraction appears to be unfavorable is also consistent with the report that in the vapor phase hydrogenation with atomic hydrogen little (<10%) or no allylic abstraction (the most labile hydrogen) takes place.[37] If allylic abstraction accounts for the formation of **1a** then products (disproportionation and combination) from the reaction of the allylic radical, **1b**, would also be observed (eq 4).



(4)

Since no diolefinic products are formed and only **1g** and **1h** are detected and since the ratio $\rho_{MDA} / \rho_{MDE} = 1$, it can be assumed that no allylic abstraction takes place.

Since the products of disproportionation can be identified, the disproportionation to combination ratio is easily determined. The value determined for the reaction carried out to low convertion (4-26% reaction) is 2.45 ± 0.07 (−78 °C). When the reaction is carried out at several temperatures, −100 °C, −78 °C, −42 °C, a plot of ln k_d/k_c vs. 1/T gives $E_{a(dis.)} - E_{a(com.)}$ equal to 1.0 kcal/mol, (see Fig. II-1). The ratio of rate constants, k_d/k_c at 25 °C, calculated from the plot is 1.01 and is identical with the value (k_d/k_c = 1.0, 1.1) reported for the secondary butyl radical.[38]

The ratio of rate constants, k_d/k_c, changes with temperature, predictably to smaller values as the temperature is increased, since at lower

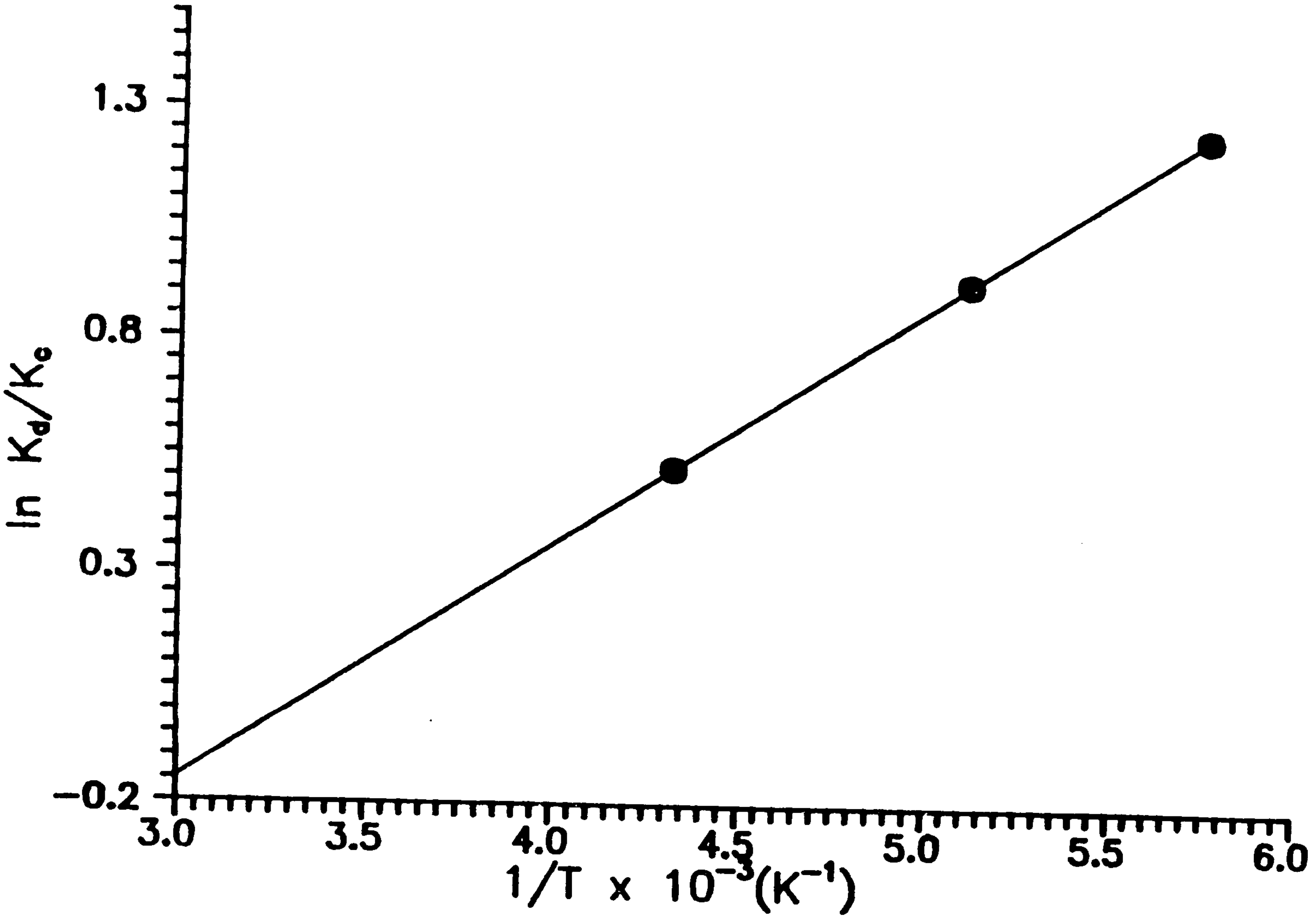


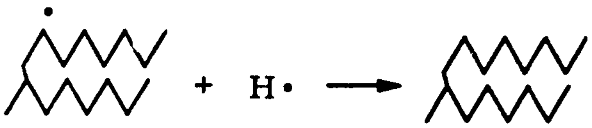
Fig. II-2. A plot of ln k_d/k_c vs 1/T for the self reactions of 1-methylheptyl radicals.

temperature (*i.e.*, high viscosity) molecular rotation is disfavored as is the rate for the disproportionation reaction.[39a,b]

Since the disproportionation to combination ratio for the products from the addition of protium or deuterium atoms will be the same, k_d/k_c determined from the reactions with deuterium was used to calculate the yields of octane and 1-protiooctene which were formed from disproportionation when the reaction of 1-octene and hydrogen atoms was carried out (see Table II-1, footnote b). The yield of the dimeric product, 7-methylpentadecane, was shown to be dependent upon the initial concentration of olefin, see Table II-3.

The concentration dependence of the yield of 7-methylpentadecane is consistent with its formation from a bimolecular reaction. It must be due to addition of the 1-methylheptyl radical to the terminal position of 1-octene (eq 5), followed by subsequent reaction of atomic hydrogen with the new secondary radical (eq 6).

(5)



(6)

The position of deuteration observed when this dimer is formed using deuterium instead of hydrogen is consistent with this proposed sequence of reactions. When the reaction is carried out with deuterium the dimer is found

Table II-3. The Products from the Reaction of Hydrogen Atoms with Acetone Solutions of 1-Octene (-78 °C)[a]

			Products (%)						
[Olefin]	Time	[1-Octene] left (%)	 [b]	 [c]	 [d]	 [d]	 [d]	 (*meso*- and *dl*-, 1:1)	
0.007	10	20.3	(27.1)	(23.8)	(31.8)	4.7	tr.	12.5	-
0.014	10	22.1	(26.8)	(23.1)	(32.1)	5.0	tr.	12.7	-
0.145	10	74.8	(25.3)	(8.3)	(37.8)	10.4	2.1	14.9	1.3
0.216	15	64.3	(22.2)	(14.4)	(35.2)	10.8	2.1	3.9	1.4

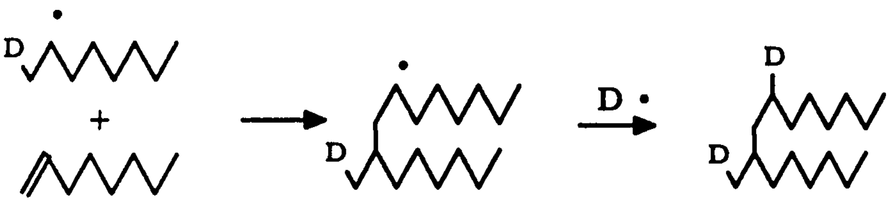
[a] H_2 low rate 4 ml/min. The products are listed in mol %.

[b] Calculated using $k_d/k_c = 2.54$; $\rho_{MDA}/\rho_{MDE} = 1$.

[c] Hydrogen addition-addition products.

[d] Disproportionation products.

to contain deuterium at the 7-methyl and on the 9-position of the pentadecane, see eq 7. The carbon centered radical addition to 1-octene to form 7-methylpentadecane was further substantiated by carrying out the reduction of a dilute solution of 1-octene (< 0.014 M). Since the addition dimer is formed by the bimolecular reaction of the secondary radical with 1-octene, the lower the concentration of olefin the less dimeric addition product will be formed. The results from the first two reactions in Table II-3 are consistent with this prediction.



(7)

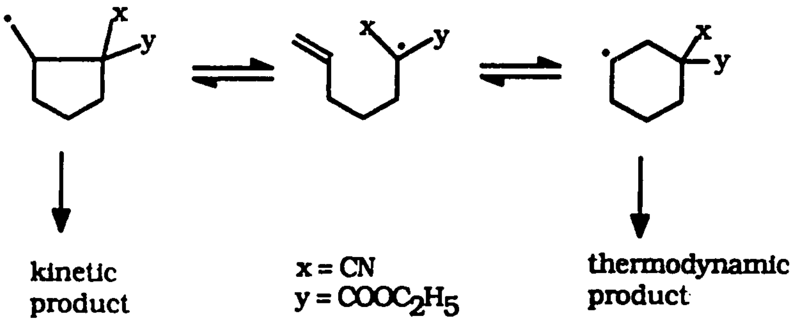
2. Reversible radical cyclization

During the last 25 years since it was first reported,[40] the ring closure reactions of the 5-hexenyl radical and its substituted analogs by intramolecular addition, have been extensively investigated.[41-50] The cyclization to give five membered rings has been widely accepted as a mechanistic probe which is characteristic of a free radical intermediate,[51-53] and has been used as a standard for the determination of the absolute rates of a wide variety of competitive free-radical reactions.[54-56]

With an understanding of the mechanism of these cyclization reactions their use as standard synthetic methodology has rapidly been established.[57-60]

The synthetic and mechanistic studies have primarily utilized tin hydride reduction as the method which promotes the cyclizations. Concentrations of tin hydride used for both mechanistic and synthetic reactions have routinely been relatively high (0.02-0.05 M) in order to sustain the chain reaction and to achieve isolable yields.[43c]

The literature contains examples of radical cyclizations which form 6-membered rings when the radical centers are stabilized by substitution.[42] The stabilized radical closes and opens reversibly and eventually yields the thermodynamically more stable 6-membered carbocyclic radical which, in a nonchain process, yields the thermodynamically more stable product (eq 8).



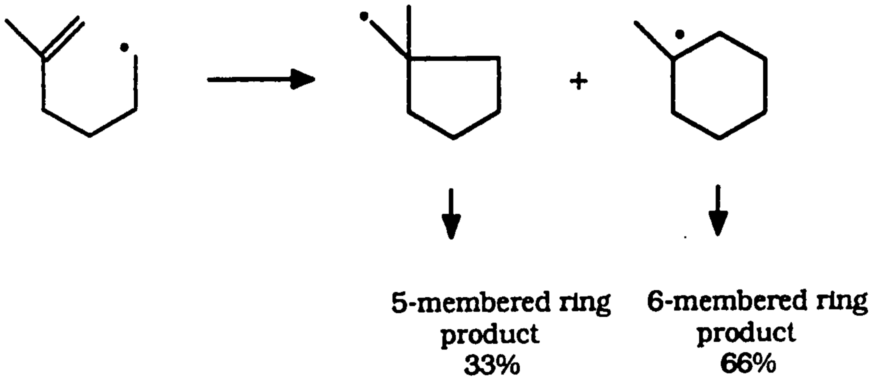
(8)

During the thermal decomposition of cyclopentylacetyl peroxide, another nonchain process, the radical cyclization appears to be reversible, since a substantial amount of 6-membered ring hydrocarbon was formed.[41] In the original studies of Walling and Cioffari, it was noted that when a low concentration of tin hydride was used, $[n\text{-Bu}_3\text{SnH}] \leq 0.02$ M, a detectable amount of 6-membered ring hydrocarbon was formed.[42c] However, under the conditions used to follow the kinetics of the reaction, the 5-membered ring was shown to be irreversibly formed (eq 9, 10).

(9)

(10)

Although it was not shown to be formed irreversibly, the radical from a disubstituted olefin also cyclizes to yield 6-membered ring products (eq 11). Closure to the 5-membered ring was presumably sterically disfavored.[61]

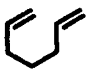
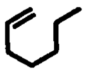
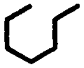
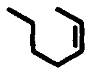
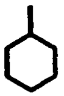
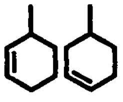


(11)

3. The cyclization of the 1-methyl-5-hexenyl radical

Since the initial addition of a hydrogen atom to a terminal olefin, 1-octene, is exclusively in the 1-position, the addition of a hydrogen atom to 1,6-heptadiene provides the opportunity to observe a radical cyclization, 5/6 membered ring, under conditions where the transfer reaction is extremely slow due to the low concentration of atomic hydrogen. Under these conditions, (–78 °C, [H·] $\cong$ 10^{-7} M, see Appendix II-1), the secondary radical resulting from the addition of a hydrogen atom to the terminal position of the diene leads to a complex mixture of products resulting from open chain and cyclized radicals, see Tables II-4, II-5 and II-6. When either deuterium or protium atoms are used, Table II-4 to II-6, it is clear that 6-membered ring products, P_6, are formed in preference to the 5-membered ring carbocycles, P_5. As the hydrogen flow rate was increased, Table II-5, the ratio of products, P_6/P_5, decreased. Although closure to the *cis*-5-membered ring is kinetically favored, reversible cyclization favors the formation of the 6-membered ring. At 25 °C, the ratio of *cis-/trans*-1,2-dimethylcyclopentane reported for the irreversible cyclization of the 1-methyl-5-hexenyl radical is 73/27.[61] The activation parameters reported ($E_{a(trans-)} - E_{a(cis-)}$ = 0.7 kcal/mol)[61] predict that at –78 °C the products should be 84/16 *cis/trans*. The reversible hydrogen atom promoted cyclization (Table II-4) shows a ratio of 28/72 at –78 °C. As expected, the irreversible product ratio of kinetic control are different than the ratio of cyclized product formed from the reversible cyclization. At low concentrations of atomic hydrogen the cyclized radical has a longer life time and ring opening takes place. A plot of the hydrogen flux *vs.* the ratio P_6/P_5 extrapolates to 1.57 at a hydrogen flow rate of zero, see Fig. II-3 (the

Table. II-4. The Reaction Products from the Reaction of 1,6-Heptadiene with Atomic Hydrogen (–78 °C)[a]

	SM	Products (% yield)[b]													
Run												 (*meso*- and *dl*-, 1:1)	 (*meso*- and *dl*-, 1:1)	Other Dimers	P_6/P_5[c]
1	95.0	0.6	2.0	0.6	-	-	-	0.2	0.8	-	0.2	0.6	-	-	1.3
2	77.0	2.0	8.9	2.4	1.7	tr	tr	0.7	2.7	tr	0.8	2.9	0.6	0.4	1.3
3	49.3	4.4	16.3	4.4	6.5	1.9	0.7	1.7	5.8	tr	1.6	3.8	2.5	1.1	1.2
4	00.0	-	0.0	0.0	-	0.0	0.0	-	-	-	0.0	0.0	(1:0.97)[d]	(0.09)[d]	

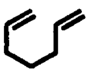
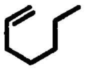
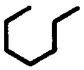
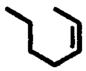
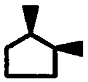
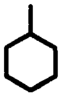
[a] [1,6-Heptadiene] = 0.074 M in acetone. H_2 flow rate 4 mL/min. The products are listed in mol%.

[b] Seven dimeric products were detected: two diene coupling products (*meso*- and *d,l*-); one diene addition product; one monounsaturated dimer and three saturated dimers, two of which were identified as *meso*- and *dl*-6,7-dimethyldodecane. The seven products were typically formed in the ratio of 1:0.9:0.5:0.7:0.04:0.3:0.3.

[c] The ratio of 6- to 5-membered ring cyclized products.

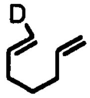
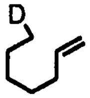
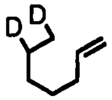
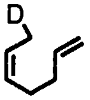
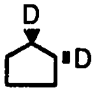
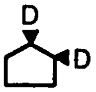
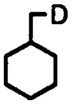
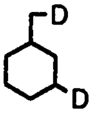
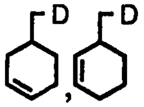
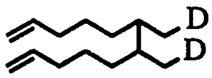
[d] The dimeric products consisted of 97% *meso*- and *dl*-6,7-dimethyldodecane and 6-methyltridecane (1:0.97:0.09).

Table II-5. The Reaction Products from the Reaction of 1,6-Heptadiene with Atomic Hydrogen (–78 °C)[a]

	SM	Products (% yield)													
H_2 flow rate (mL/min)										Et 		 (*meso*- and *dl*-, 1:1)	 (*meso*- and *dl*-, 1:1)	Others[d]	P_6/P_5[e]
4/3.5[b]	80.1	1.2	6.6	2.4	1.6	0.5	0.2	0.8	2.2	0.2	0.8	1.9	0.6	1.0	1.6
20[c]	53.9	4.7	11.9	4.0	5.9	1.6	0.7	2.1	5.9	0.3	1.8	3.7	1.9	1.7	1.1

[a] Concentration in acetone (0.1035 M). The products are listed in mol%.
[b] 4 ml/min. of H_2 (3.5 min.).
[c] 20 ml/min. of H_2 (1.5 min.).
[d] Other dimers, see Table I-4.
[e] The ratio of 6- to 5-membered ring cyclized products.

Table II-6. The Products from the Reaction of Deuterium with 1,6-Heptadiene (–78 °C)[a]

		Product %	Proposed Mechanism[c]
H		12.5	D atom addition - disproportionation
S		26.3	D atom addition - disproportionation
J		8.8	D atom addition - D atom addition
K	 (*trans-* + *cis-*)	11.4	D atom addition - disproportionation
L		6.0	D atom addition - cyclization - D atom addition
M		5.3	D atom addition - cyclization - D atom addition
N		3.9	D atom addition - cyclization - disproportionation
O		7.0	D atom addition - cyclization - D atom addition
P,Q		5.8	D atom addition - cyclization - disproportionation
R	 (*d,l-* and *meso-*, 1:1)	13.1	D atom addition - combination

[a] Concentration in acetone (0.16 M). H_2 flow rate 4 mL/min. The products are listed in mol%.

[b] Conversion = 3.1%.

[c] $P_6/P_5 = 1.46$, $\rho_{MDA}/\rho_{MDE} = 1.02$, $k_d/k_c = 2.30$.

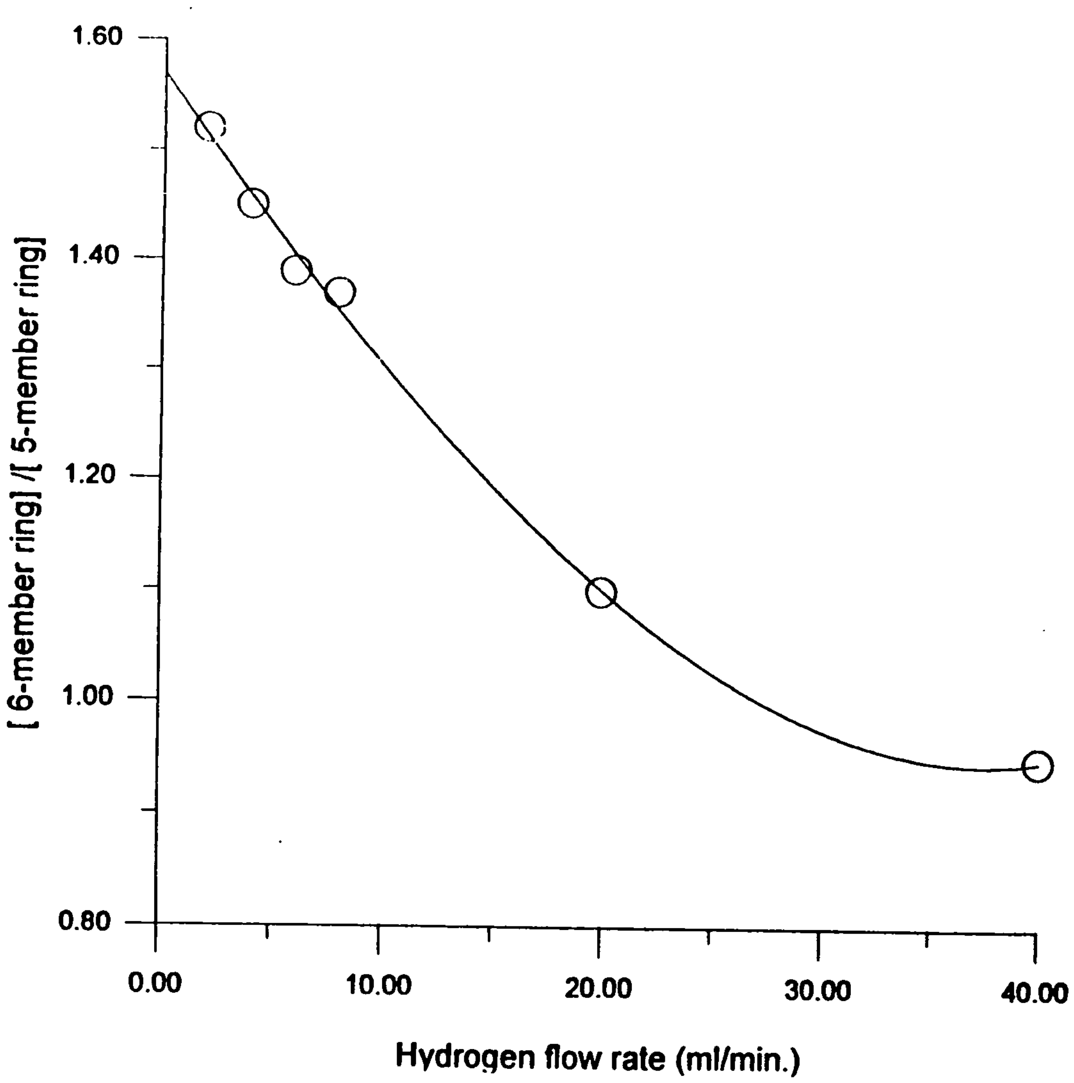
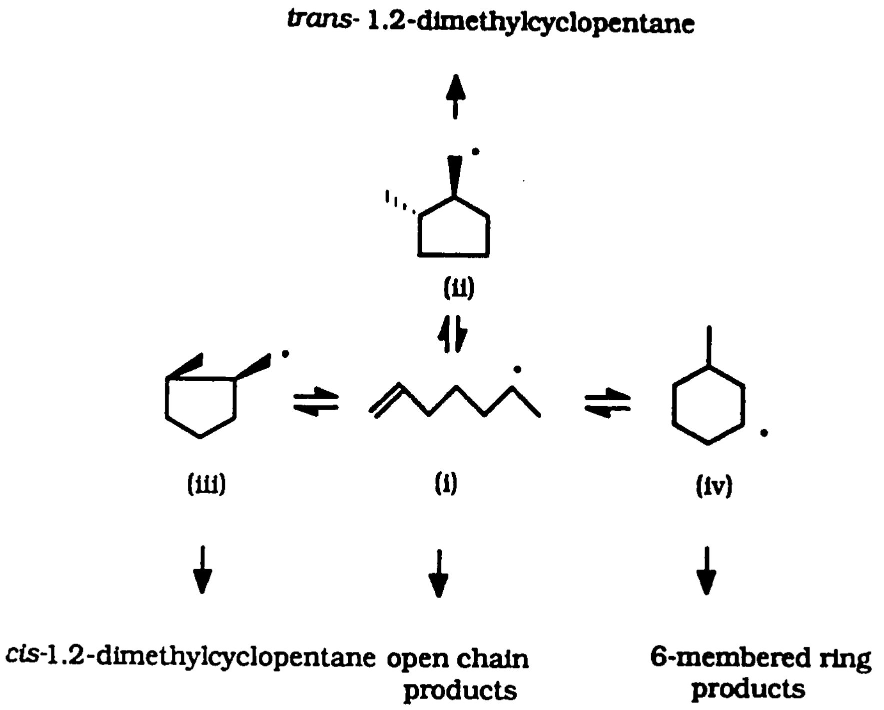


Fig. II-3. A plot of the hydrogen flow rate vs. the ratio of 6-/5-membered ring products.

flow rate of zero, see Fig. II-3(the concentration of 1,6-heptadiene in acetone is 0.1 M). If the cyclization is truly reversible, an equilibrium distribution of products will eventually be established, see Scheme II-1.



(12)

Scheme II-1

Unfortunately, equilibrium cannot be reached since very fast bimolecular reactions: combination, disproportionation, and reaction with H•, $k \cong 10^9\ M^{-1}\ sec^{-1}$, remove the radicals, i-iv, from the equilibrium. These reactions appear to be competitive with the reversible cyclizations since the product ratios are dependent on the concentrations of H•, see Table II-5. When the hydrogenation was carried out to higher conversion (Table II-4, reaction 2,3), the product mixture contained 5-membered ring, 6-membered ring, and open chain hydrocarbons. The dimeric products derived from the open chain radicals are *meso*- and *d,l*-6,7-dimethyl-1,11-dodecadiene and 6-methyl-1,12-tridecadiene. The three dimers are formed in a ratio of 1:0.9:0.5. At these higher conversions the primary products are further reduced to a monoolefinic dimer and three saturated dimers. Two of the saturated dimers were identified as *meso*- and *d,l*-6,7-dimethyldodecane (0.4:0.3). The dimeric products are formed in a ratio of approximately 1 : 0.9 : 0.5 : 0.7 : 0.1 : 0.04 : 0.3, see Table II-4. Complete hydrogenation of the reaction mixture established that >97% of the dimeric products were *meso*- and *d,l*-6,7-dimethyldodecane and 6-methyltridecane, see Table II-4, reaction 4.

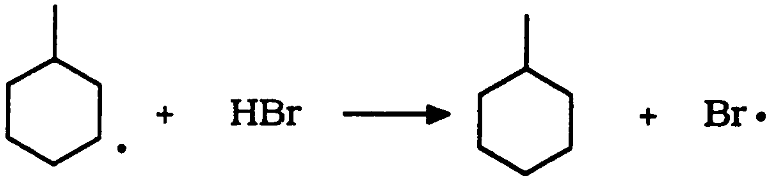
When the reduction of 1,6-heptadiene was carried out with deuterium, but at very low conversion (3.1%) and low concentration (0.16 M), only two dimeric products were detected, *d,l*- and *meso*-6,7-di(deuteromethyl)-1-11-dodecadiene, see Table II-6. The distribution of deuterium in the product mixture can be obtained by analysis of its mass spectrum, gas chromatograph, and its ^{1}H and ^{2}H NMR.

The mass spectrum (GC/MS) of the product mixture showed that it contains: 1,6-heptadiene (d_1, H), 1-heptene (d_1, S), 1-heptene (d_2, J), *trans*- and *cis*-1,5-heptadiene (d_1,K), *trans*-1,2-dimethylcyclopentane (d_2, L), *cis*-1,2-dimethylcyclopentane (d_2, M), methylcyclohexane (d_1, N), methylcyclohexane (d_2, O), 4-methylcyclohexene (d_1, P), 3-methylcyclohexene (d_1, Q), 6,7-dimethyl-1,11-dodecadiene (d_2, R). Again, as in the case of the reactions of 1-octene, if the initial reaction is regiospecific addition to the terminal position of 1,6-heptadiene, then the radicals, i-iv, are formed by reversible cyclization, and the deuterated products are those listed in Table II-6. The ^{2}H NMR showed absorptions with intensity, I_n: δ 1.00 (DCH$_2$-, I_1), 1.40 (-DCH-, I_2), 1.65 (DCH$_2$-CH=CH-, I_3), and 5.10 (DCH=CH-, I_4). From the concentrations of the products (GC), the distribution of the deuterated products is calculated. The proportionality constant, f, was obtained from the equation, $I_3 = [K]/f$. Using the following relationships: $[H] = fI_4$, $[J] = fI_3\text{-}[O]$, $[S] = fI_1\text{-}2[L+M+R]\text{-}fI_2\text{-}[N]\text{-}[P]\text{-}[Q]$, the distribution of monodeuterated products was obtained.

It was not obvious, however, that the 6-membered ring radical, iv, is in fact reversibly formed. To test the assumption that (iv) is formed reversibly, advantage was taken of the previously made observation that alkyl bromides are dehalogenated during their reaction with atomic hydrogen, eq 13.[37,62]

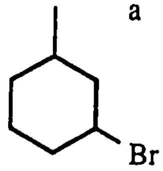
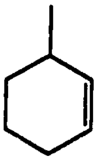
$$RBr + H\bullet \rightarrow R\bullet + HBr \qquad (13)$$

When 1-bromo-3-methylcyclohexane was allowed to react with atomic hydrogen it formed, among other products, heptane (see Table II-7). The formation of the saturated alkane via radical (i) is expected since $k_{addition} >> k_{abstraction}$ (*i.e.*, for either abstraction of a bromine atom or a hydrogen atom).[63] The yield of heptane resulting from the reactions of radical (i) is limited since not only is the ring opening of (iv) expected to be slow, but its rapid reversal with HBr should give a large amount of the dehalogenated product, methylcyclohexane, eq 14, (see Table II-7).



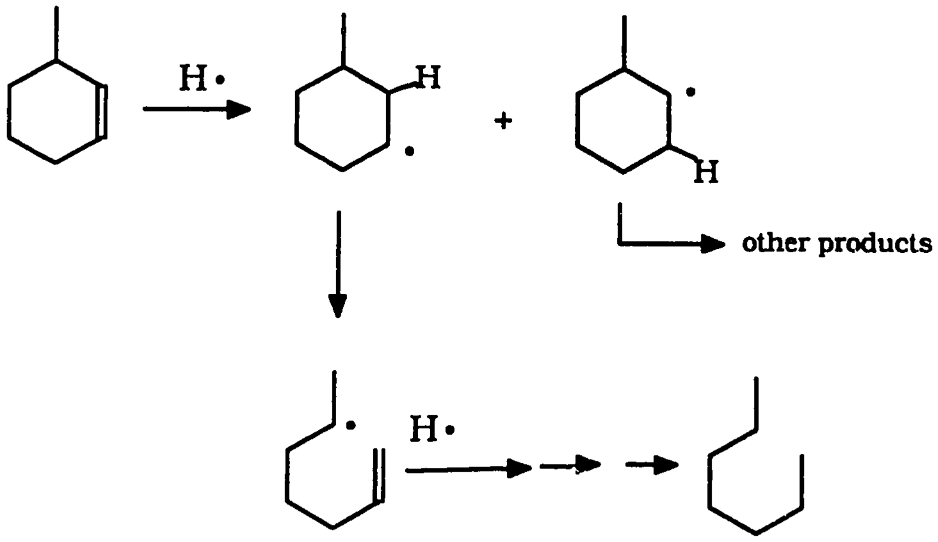
(14)

Table II-7. The Hydrogen Promoted Ring Opening Reactions of the 3-Methylcyclohexyl Radical (–78 °C)

Substrate	Products (yield, %)		S.M. (%)
 [a]	heptane methylcyclohexane dimer	3.1 55.9 19.8	21.5
 [b]	heptane methylcyclohexane dimer	0.1 47.9 51.6	0.4

[a] 1.1 M in acetone, H_2 20 mL/min, 60 min.
[b] 0.2 M in acetone, H_2 2 mL/min, 60 min.
[c] The products are listed in mol%.

The 3-methylcyclohexenyl radical, iv, can be generated by the addition of atomic hydrogen to 3-methylcyclohexene, eq 15. In this reaction a small amount of heptane is also formed (see Table II-7).



(15)

Conclusions

The solution phase addition of the hydrogen atom to a terminal olefin (−78 °C) is regiospecific, *i.e.* addition is exclusively to the terminal carbon. The addition of hydrogen to 1,6-heptadiene generates the 1-methyl-5-hexenyl radical at concentrations of less than 10^{-7} mol/L. This secondary radical either reacts with atomic hydrogen, undergoes combination or disproportionation, adds to another olefin, or reversibly cyclizes. The cyclized radical which yields *cis*-1,2-dimethylcyclopentane, however, under the reaction conditions is formed reversibly. The open radical recyclizes to the more stable *trans*-5-membered ring and 6-membered ring radicals, see equation 12. Although the radical intermediates are all reversibly formed, an equilibrium mixture of products is never reached since subsequent fast reactions no doubt remove the intermediates from the reaction media.

Experimental

1. General method for the H atom reactions.

The substrate is placed in the Pyrex reactor (85 mL), see Fig II-4. Helium and hydrogen or deuterium are introduced into the system through fine valves 1 and 2, which control the flow rate, and switch valves S_1 and S_2, which open or close the inlets. Gauge 1 and gauge 2 are used to read the pressure coming out from the gas cyclinders. Hydrogen or deuterium gas flow rates are measured in the following manner: (1) the reactor is taken apart; (2) the inlet of the flow meter is connected to the system; (3) valve 2 is adjusted to obtain the desired flow rate. Ethanol/dry ice (–78 °C), acetonitrile/dry ice (–42 °C) or diethyl ether/dry ice (–100 °C) are used to control the reactor temperature. The pressure of the reaction system is measured by a digital manometer (MKS Baratron Type 170 Meter, MKS Instruments, Inc.) which is read with a MV meter to ± 0.01 torr. The reactor outlet is connected to a cold trap (–78 °C) to prevent substrate contamination of the pump. Cooling air is passed into the microwave cavity to prevent the temperature from rising due to the heat generated in the discharge cavity. The microwave cavity is placed 4 cm above the surface of the reaction substrate.

The reaction is started by first opening helium gas valve S_1, keeping S_2 closed and monitoring valve 1 to adjust the system pressure to 3.00 torr (gauge 3). The microwave generator is turned on, and the output is adjusted in the range of 50-80%. The plasma is ignited by Tesla coil with a yellow flame indicating He plasma. The valve S_2 is opened to introduce hydrogen

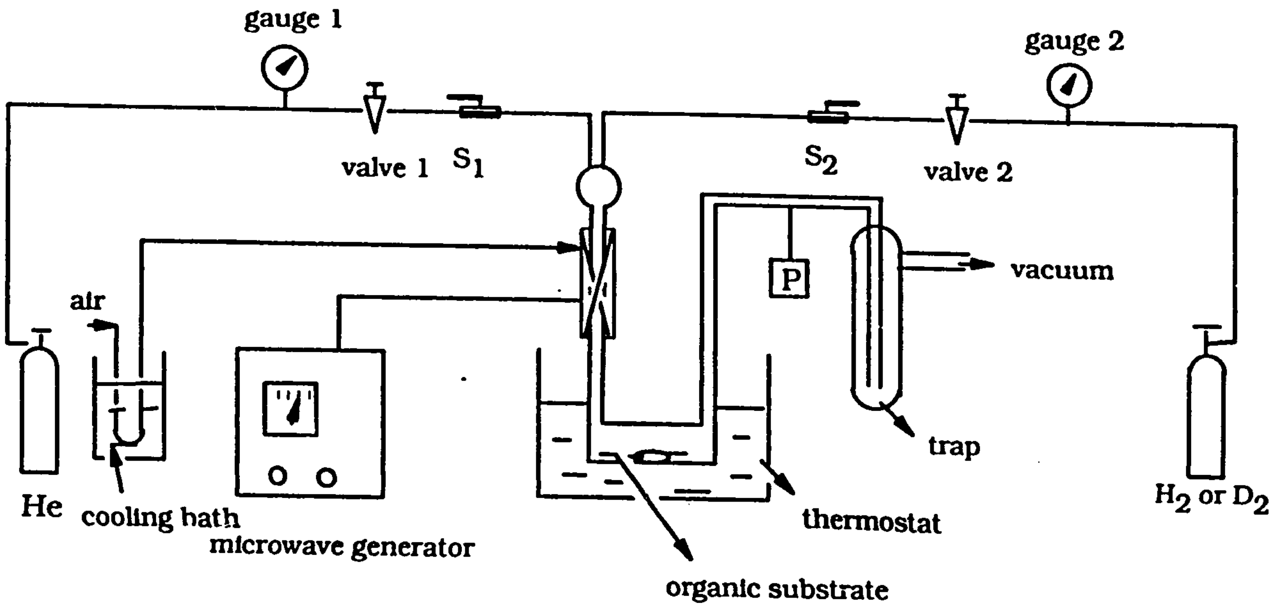


Fig. II-4. Diagram of apparatus for H atom reaction into the system which causes the flame colour to change from yellow to purple. For each reaction, the U-shaped reactor is cleaned with a chromic acid solution, water, concentrated ammonium hydroxide, and distilled water, and then oven dried (200 °C).

2. Instrumentation.

The ^1H, ^2H, and ^{13}C NMR were obtained using either a Bruker WH-200 (200 MHz), Bruker AM-300 (300 MHz) or Bruker AM-400 (400 MHz) NMR spectrometer. Unless otherwise indicated, the ^1H NMR are referenced to TMS as an internal standard at 0.00 ppm or to the residual $CHCl_3$ in $CDCl_3$ as an internal standard at 7.26 ppm. The ^{13}C NMR chemical shifts were reported in δ (ppm) relative to chloroform (δ $CDCl_3 = 77.0$). The ^{13}C NMR were studied by APT (attached proton test) to determine the number of protons attached to each carbon. Gas chromatograph-infrared spectral (GC/IR) data were obtained using a HP 5965A IRD instrument interfaced to a HP 5890 gas chromatograph (Hewlett Packard) fitted with a DB-5 (30 m x 0.25 mm) glass capillary column. Gas chromatograph-mass spectral (GC/MS) data were obtained using a Varian Vista 6000 gas chromatograph fitted with a glass capillary column, DB-5 (30 m x 0.25 mm, J&W Scientific), and coupled to a VG-70E mass spectrometer with a 1125 Data System. The isotopic content of the products was conveniently determined from GC/MS and ^2H NMR spectra. In order to avoid possible error due to partial separation of the isotopic mixtures by GC, the mass fragmentography technique was employed. Thus, the total ion mass of each compound (m/z) was integrated for each GC peak and used as the numerical value for the analytical calculations. GC analyses were carried out on a Varian Vista 6000 gas chromatograph fitted with a flame ionization detector. The instrument was interfaced to a Varian Vista CDS 401 chromatograph data system. To quantitatively calculate the yield of the reaction products, a standard solution of known concentrations of the authentic products and an internal standard was prepared and analyzed by GC. The concentrations of the standard mixture were as close to the concentration of the actual reaction mixture as possible. The initial concentrations of the substrate I and internal standard S are Ci and Cs. A standard mixture of substrate Ci^o, internal standard Cs^o, and product Cp^o was analyzed to give the areas: Ai^o; As^o; Ap^o. The reaction mixture was then analyzed to give the areas: Ai; As; Ap. The yields of the product P and the recovered I were calculated using the following equations:

$$P\% = [(Ap/As)/(Ap^o/As^o)][(Cp^o/Cs^o)][Cs/Ci] \times 100\%$$

$$I\% = [(Ai/As)/(Ai^o/As^o)][(Ci^o/Cs^o)][Cs/Ci] \times 100\%$$

Several injections of each solution were carried out to obtain the average relative area ratios. The products were identified by a comparison of their retention times, GC-IR and GC/MS with those of authentic samples. If authentic compound was not avalible, ^1H NMR, ^{13}C NMR and APT were obtained.

Two columns were used in the GC analyses: Rtx-1 (105 m × 0.25 mm × 0.5 m, RESTEK corporation) capillary column; PONA (50 m × 0.21 mm × 0.5 m).

3. Materials.

Acetone (reagent grade, BHD Inc.) was dried over anhydrous potassium carbonate and distilled prior to use. 1-Octene (Phillips Petroleum Company, research grade, 99+%) was checked by GC before use. *n*-Octane (Aldrich, 99+%), *trans*-2-octene and *cis*-2-octene (Phillips Petroleum Company, research grade, 99+%) were used as received. 1,6-Heptadiene (Aldrich, 99%) was checked by GC and found to be > 99% pure. Deuterium gas was obtained from Matheson Gas Products Canada and used as received. Hydrogen gas (LINDE union carbide) was used as supplied.

***cis*- and *trans*-1-Bromo-3-methylcyclohexane** (1:4) were prepared according to the literature procedure.[64] The product was isolated in 63% yield: bp 73-78 °C/32 mm Hg; ^{1}H NMR (200 MHz, $CDCl_3$): 0.90 (d, 3H, J = 6.5 Hz), 1.40-2.10 (m, 9H), 4.65 (m, 1H). Anal. Calcd for $C_7H_{13}Br$: C, 47.46; H, 7.34; Br, 45.20. Found: C, 47.50; H, 7.34; Br, 44.99.

4. Identification of the Product.

The following products were identified by a comparison of their GC retention times, GC/IR and GC/MS with those of authentic samples: ***n*-octane, *trans*-2-octene, *cis*-2-octene, 1-heptene, heptane, *trans*-2-heptene, *cis*-2-heptene, methylcyclohexane, ethylcyclopentane, 3-methylcyclohexene** and **4-methylcyclohexene.**

***dl*- and *meso*-7,8-Dimethyltetradecane** were obtained by preparative glpc collection (100 °C, 10 ft × 1/4 in. SE-30 column) from the product mixture resulting from atomic hydrogen addition to 1-octene. A mixture of *dl*- and *meso*-7,8-dimethyltetradecane was obtained. GC, GC/MS and GC/IR showed two isomers in a 1:1 ratio: ^{1}H NMR (400 MHz, $CDCl_3$): 0.73 (d, 3H, J = 6.6 Hz), 0.82 (d, 3H, J = 6.6 Hz), 0.89 (t, 6H, J = 6.6 Hz), 1.27 (m, 22H); ^{13}C NMR (300 MHz, $CDCl_3$): 14.18 (C-1, *dl-* and *meso-*), 14.49, 16.54 (C-15, *dl-, meso-*), 22.79, 32.06 (C-2, C-3, *dl-* and *meso-*), 27.77, 27.83 C-5, (*dl-* and *meso-*), 29.79, 29.82 (C-4, *dl-* and *meso-*), 32.00, 35.04 (C-6, *dl-* and *meso-*), 36.68, 37.64 (C-7, *dl-* and *meso-*). The mass spectrum had a molecular ions at m/z = 226 expected for M^+ of $C_{16}H_{34}$.

7-Methylpentadecane was prepared according to the literature procedure.[65] CuI (0.677 g, 3.54 mmol) was placed in a 40 mL centrifuge tube, capped with a serum stopper, and flame dried under a stream of Ar. Ether (20 mL) was added to the tube, and the resulting suspension was cooled to −50 °C. At this temperature, an etheryal solution of *sec*-octyllithium (4.0 mL, 0.80 g, 7.08 mmol) was added, prepared from the reaction of lithium and 2-chlorooctane. The tube was shaken vigorously for 5 min. keeping the temperature between −50 and −20 °C. Centrifugation at −78 °C separated the resulting suspension into a small quantity of solid and a solution (two layers). The solution was taken into another tube for the next reaction. An ether solution (1 mL) containing 1 mmol of 1-bromooctane was added in one portion to a solution of 5 mmol of lithium dialkylcuprate in 5 mL of ether at −78 °C. The mixture was allowed stand for 1hr at −25 °C with occasional swirling. An aqueous solution of NH_4Cl was added to quench the reaction. The organic phase was washed with a saturated NaCl solution, dried with Na_2SO_4, and analyzed by GC. Distillation gave 0.1 g (55%) of 7-methylpentadecane: ^{1}H NMR (400 MHz, $CDCl_3$): 0.84 (d, 3H, J = 6.6 Hz), 0.89 (t, 6H, J = 6.6 Hz), 1.27 (m, 25H). The mass spectrum had a molecular ion at m/z = 226 expected for $C_{16}H_{34}$. 7-Methylpentadecane in the product mixtures was identified by a comparison of the GC retention times, GC/IR and GC/MS with the above synthesized sample.

***trans-* and *cis*-1,2-Dimethylcyclopentane** were obtained by the reactions of 6-bromo-1-heptene with tributyltin hydride[42c] and identified by their GC/MS[66] and GC/IR[67] which were identical with those reported in the literature. 6-Bromo-1-heptene was prepared according to the literature precedure[43c,68]: bp 79 °C (20 mm Hg); ^{1}H NMR ($CDCl_3$) 1.61-2.22 (m, max. 1.70, 9H), 4.10 (m, 1H), 4.71-5.10 (m, 2H), 5.41-6.10 (m, 1H); IR: 3080, 2960, 1640, 1440, and 1375cm^{-1}. *trans-* and *cis*-1,2-Dimethylcyclopentane in the product mixture from the addition of atomic hydrogen to 1,6-heptadiene were identified by a comparison of their GC retention times and GC/MS and GC/IR with the above synthesized compounds.

***trans-* and *cis*-1,5-Heptadiene** were prepared according to the literature procedure:[36] bp 92 °C/701 mm Hg (lit.[36] 94.0-94.5/760 °C mmHg); ^{1}H NMR (300 MHz. $CDCl_3$): 1.68 (d, 3H, J = 4 Hz), 2.10 (m, 4H), 4.85-5.10 (m, 2H), 5.60-5.90 (m, 1H), 5.40 (m, 2H). The GC/MS and GC/IR of *trans*-1,5-heptadiene were identical with those reported in the literature.[66-67] The GC/MS of *cis*-1,5-heptadiene was identical with the spectra reported in the literature.[66] IR (gas phase) ν 3083, 3021, 2830, 1831, 1642, 1445, 993, 916 and 698 cm^{-1}.

***dl-* and *meso*-6,7-Dimethyl-1,11-dodecadiene** were isolated by preparative glpc collection (100 °C, 10 ft × 1/4 in. SE-30 column) from the product mixture resulting from atomic hydrogen addition to 1,6-heptadiene and were identified by their ^{1}H NMR , ^{13}C NMR and APT, GC/MS and GC/IR. A mixture of *dl-* and *meso*-6,7-dimethyl-1,11-dodecadiene was obtained. GC, GC/MS and GC/IR showed two isomers in a 1 : 1 ratio: ^{1}H

NMR (300 MHz, $CDCl_3$): 0.73 (d, 3H, J = 6.6 Hz), 0.82 (d, 3H, J = 6.6 Hz), 1.20-1.40 (m, 10H), 2.0 (m, 4H), 4.88-5.10 (m, 4H), 5.70-5.88 (m, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): 14.39, 16.44 (C-13, *dl-*, *meso-*), 27.07, 27.11 (C-4, *dl-* and *meso-*), 32.42, 34.16 (C-5, *dl-* and *meso-*), 34.39, (C-3, *dl-* and *meso-*), 36.49, 37.46 (C-6, *dl-* and *meso-*), 114.12 (C-1, *dl-* and *meso-*), 139.20 (C-2, *dl-* and *meso-*). m/z (M^+, 194); IR (gas phase): ν 2970, 2933, 2876 (st, 1.8:2.1:1) cm^{-1}; 1383, 1464 (w) cm^{-1}.

***dl-* and *meso*-6,7-Dimethyldodecane** were isolated by preparative glpc collection (100 °C, 10 ft × 1/4 in. SE-30 column) from the product mixture resulting from atomic hydrogen addition to 1-heptene. Their structures were assigned from an analysis of their ^1H NMR, ^{13}C NMR and APT, GC/MS and GC/IR. A mixture of *dl-* and *meso*-6,7-dimethyldodecane was obtained. GC, GC/MS and GC/IR showed two isomers in a 1:1 ratio: ^1H NMR (300 MHz. $CDCl_3$): 0.74 (d, 3H, J = 6.6 Hz), 0.81 (d, 3H, J = 6.6 Hz), 0.89 (t, 6H, J = 6.6 Hz), 1.18-1.41 (m, 18H); ^{13}C NMR (300 MHz, $CDCl_3$): 14.17 (C-1, *dl-* and *meso-*), 14.48, 16.53 (C-13, *dl-* and *meso-*), 22.79 (C-2, *dl-* and *meso-*), 27.50, 27.53 (C-4, *dl-* and *meso*), 32.32, 34.96 (C-5, *dl-* and *meso-*), 32.36, 32.94 (C-3, *dl-* and *meso-*), 36.67, 37.62 (C-6, *dl-* and *meso-*); IR (vapor) ν 2960, 2933, 2876 (st, 1:2.4:1.8); 1642, 1382 (w, 2:1) cm^{-1}. The mass spectrum had a molecular ion at m/z = 198 expected for $C_{14}H_{30}$. 6,7-Dimethyldodecane in the product mixture was identified by a comparison of the GC retention times, GC/IR and GC/MS with the above compounds.

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66 "MIST/EPA/MSDS Mass Spectral Data Base", 1990, PC Version 3.0.

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CHAPTER 3

The Regioselective Addition of Atomic Hydrogen to a Trisubstituted Ethylene. Cyclization of a Three Membered Ring by S_H1 Displacement.

*. A version of this chapter is in preparation for publication.

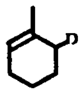
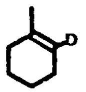
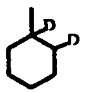
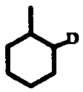
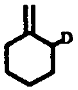
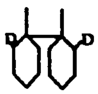
Since H atoms add to 1-octene exclusively at the terminal position of the double bond to give the 1-methylheptyl radical, an analysis of the reaction products from this secondary radical enabled us to calculate the ratio of disproportionation to combination, k_d/k_c, see Chapter 2. An attempt was made to determine the secondary/tertiary regioselectivity by carrying out the addition of atomic hydrogen to 1-methylcyclohexene.

Results and Discussion

1. Regioselective addition to 1-methylcyclohexene

When atomic deuterium was passed over neat 1-methylcyclohexene, the products of the reaction were 6-deuterio-1-methylcyclohexene (U), 2-deuterio-1-methylcyclohexene (V), 1,2-dideuteriomethylcyclohexane (W), 2-deuteriomethylcyclohexane (X), 2-deuteriomethylenecyclohexane (Y), 2,2'-dideuterio-1,1'-dimethyldicyclohexyl (Z) and four other minor dimeric products, see Table III-1. The monodeuterated monomers, both alkanes and alkenes, were no doubt the products of disproportionation. The high $1^o/2^o$ regioselectivity for the addition of atomic hydrogen to 1-octene suggested that a very large $2^o/3^o$ regioselectivity would occur during the H atom addition to 1-methylcyclohexene. If the assumption is correct that the initial reaction is regiospecific addition to the secondary position of 1-methylcyclohexene, then the deuterated products are those listed as Table III-1. Similar protiated product ratios were obtained for the reaction carried out with atomic hydrogen, Table III-2. By comparing the mass, ^1H and ^2H NMR spectra of the protiated products with the deuterated products of the reaction mixtures, it is apparent that each of the products, monomer or

Table III-1. The Product Distribution from the Addition of Deuterium Atom to 1-Methylcyclohexene[a,b]

		Products (mol%)								
Temp.(°C)	Reaction (%)	 U	 V	 W	 X	 Y	 Z	Others[c]	ρ_{MDO}/ρ_{MDB}	k_d/k_c
-78	2.0	15.3	7.9	20.2	39.4	15.3	1.5	0.5	1.02	26.2
	2.2	13.8	9.9	22.0	38.0	14.2	1.4	0.7	1.00	27.1
	5.0	14.8	6.2	20.8	40.7	15.6	1.4	0.6	1.11	29.0
	5.3	15.1	9.5	18.2	37.9	17.0	1.3	1.0	0.91	29.2
-100	2.1	15.4	7.7	20.7	41.4	13.0	1.0	1.0	1.15	41.4
	2.5	16.3	9.9	18.1	40.3	13.7	0.9	0.8	1.01	44.8
	5.7	16.1	9.4	20.7	37.5	14.8	0.8	0.7	0.93	46.9
	6.0	14.1	6.9	20.8	41.5	15.1	0.8	0.7	1.15	51.9
									1.03±0.07	

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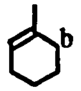
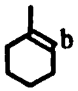
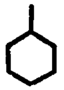
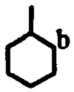
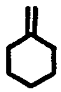
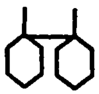
[a] Reactions were carried out in neat 1-methylcyclohexene. Reaction times are 3 or 5 minute.

[b] The product distribution was calculated by using GC and ^2H NMR analysis.

[c] Five dimeric products were detected. The five products were typically formed in a ratio of 0.3:0.2:0.2:0.3:1.

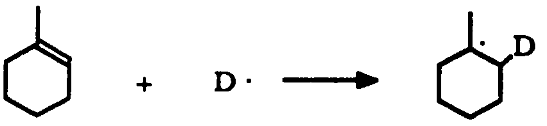
Table III-2. The Product Distribution from the Addition of Hydrogen Atom to 1-Methylcyclohexene[a,b]

			Products (mol%)								
Temp.(°C)	Time (min.)	Reaction (%)	 b U'	 b V'	 W'	 b X'	 Y'	 Z'	Others	P_{MDD}/P_{MDE}	k_d/k_c
-78	10	9.8	14.6	9.5	23.2	37.2	13.1	1.3	1.1	1.00	28.6
	20	15.9	16.2	8.5	15.2	41.0	16.2	1.5	1.3	1.00	27.2

[a] Reactions were carried out in neat 1-methylcyclohexene.

[b] Calculated using the data from Table III-1. Products formed by disproportionation reactions.

dimer, contained at least one deuterium attached to the 2-position attributable to the original olefin, see Table III-1. The mass spectra of the deuterated products showed 1-methylcyclohexene (d_1, U and V), methylcyclohexane (d_2, W), methylcyclohexane (d_1, X), methylenecyclohexane (d_1, Y), and 1,1'-dimethylcyclohexyl (d_2, Z). The ^2H NMR spectrum(see Fig. III-1) showed absorption with intensity, I_n: δ 0.83 (2a deuterium of methylcyclohexane, I_1), 1.25 (1 deuterium of methylcyclohexane, I_2), 1.55-1.60 (2e deuterium of methylcyclohexane, I_3), 1.82 (6 deuterium of 1-methylcyclohexene, I_4), 2.05 (2 deuterium of methylenecyclohexane, I_5), and 5.33 (2 deuterium of 1-methylcyclohexene, I_6). The ratio of dideuterated (W) and monodeuterated (X) methylcyclohexane was determined from an analysis of the GC/MS. From the concentration of the products, the distribution of the deuterated products was calculated in a similar manner as was done for 1-octene, see Chapter 2. The proportionality constant was obtained from the equation, $I_5 = [Y]/f$, and the deuterated product concentrations were calculated from the following relationship: $U = fI_4$, $V = fI_6$, $W = fI_2$. The first step in the addition of H atom to 1-methylcyclohexene was no doubt addition to the secondary position of the double bond to give a tertiary radical **3a** (eq 1). When **3a** encountered another deuterium radical, 1,2-dideuteriomethylcyclohexane was formed (eq 2).



3a

(1)

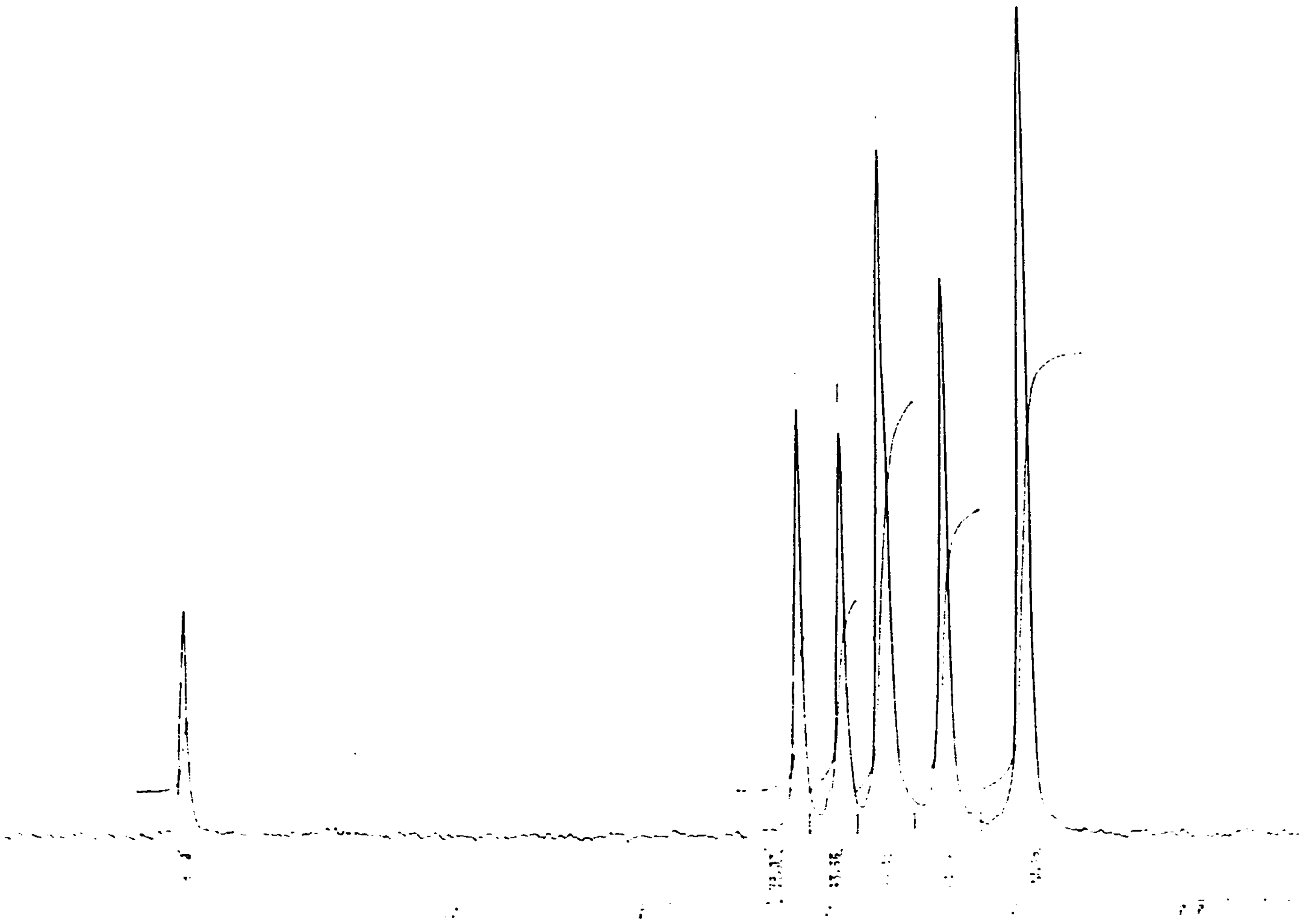
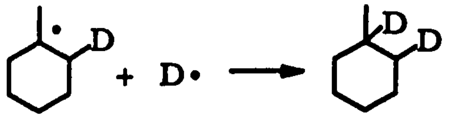
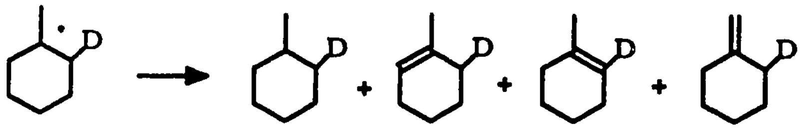


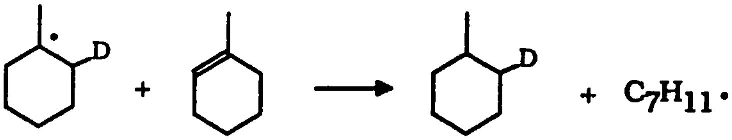
Fig. III-1. The ^{2}H NMR spectrum of the product mixture obtained from the addition of deuterium atom to 1-methylcyclohexene.

 (2)

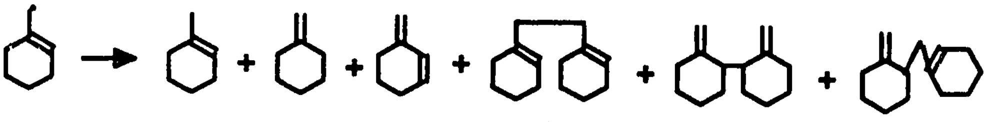
3a

The major saturated hydrocarbon contained only one deuterium. The monodeuterated methylcyclohexane can either be formed by disproportionation (eq 3) or allylic abstraction (eq 4).

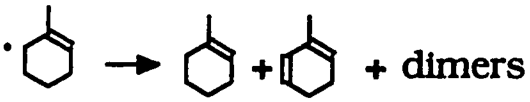
 (3)

 (4)

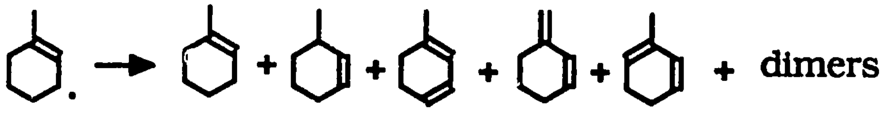
Disproportionation would give equal amounts of monodeuterated methylcyclohexane and monodeuterated olefin. The results in Table III-1 showed that the ratio of monodeuterated methylcyclohexane to monodeuterated olefin, (ρ_{MDA}/ρ_{MDE}) equals 1.03 and was consistent with the disproportionation pathway. If there were any allylic abstraction from 1-methylcyclohexene, then products from the reaction of the allylic radicals would also be observed (eq 5, 6, 7). Since the product ratio, ρ_{MDA}/ρ_{MDE}, was approximately unity and since no diolefinic products were formed and only 1-methylcyclohexane, methylenecyclohexane (monomer), and five saturated dimeric products were formed, it is unlikely that any appreciable allylic abstraction had taken place, see Table III-1. One of the saturated dimers was identified as 1,1'-dimethyl-1,1'-bicyclohexyl. The dimeric products were formed in a ratio of approximately 0.3:0.2:0.2:0.3:1, see Table III-1.



(5)



(6)



(7)

Since the products of disproportionation can be identified, the disproportionation to combination ratio was easily determined. The experiments were limited to low conversions where the yield of primary products were formed in low concentration to avoid further reaction with hydrogen atoms. The value of k_d/k_c were determined for reactions carried out at −78 °C and −100 °C. A plot of $\ln(k_d/k_c)$ *vs.* 1/T gave $E_{a(dis.)} - E_{a(com.)} = 1.52$ kcal/mol, see Fig. III-2. The ratio of rate constants, k_d/k_c, calculated from the plot at 25 °C is 7.3 and was nearly identical to the value ($k_d/k_c = 7.2$) reported for the tertiary butyl radical.[1] The calculated ratio, k_d/k_c, further substantiates the conclusion that the disproportionation

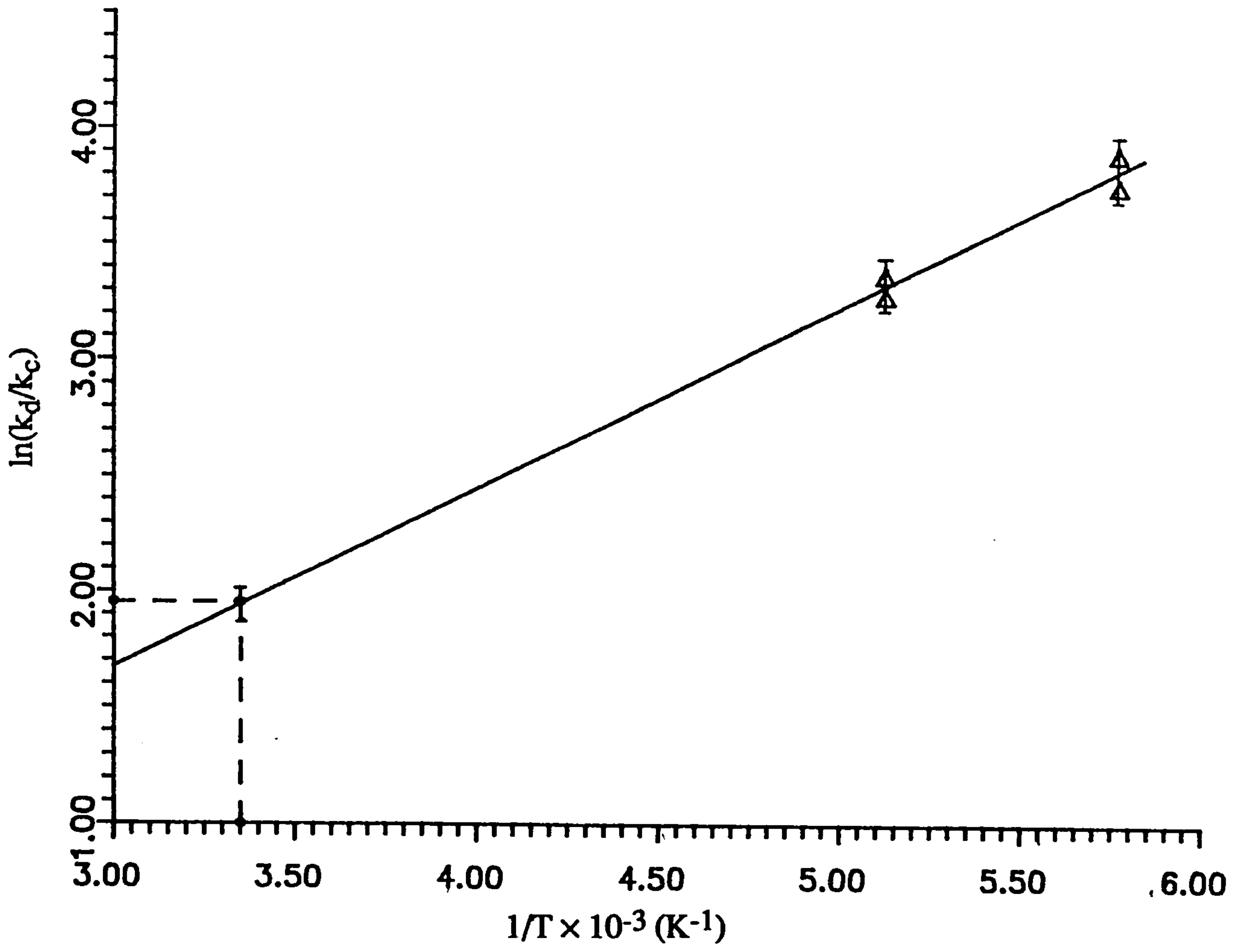
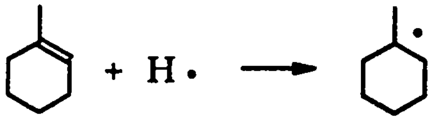


Fig. III-2. A plot of ln k_d/k_c vs 1/T for the self reactions of 1-methylcyclohexyl radical.

and combination pathway determines the formation of the products.

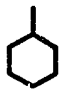
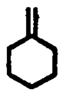
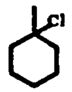
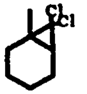
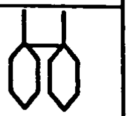
2. The reaction of atomic hydrogen with 1-methylcyclohexene in the presence of carbon tetrachloride.

In order to substantiate whether atomic hydrogen adds exclusively to the 2-position of 1-methylcyclohexene, the addition reaction was carried out in acetone containing varying concentrations of a transfer agent, carbon tetrachloride. The product distributions of the reactions were shown in Table III-3. Traces of HCl were detected by titration; however, the results of a control experiment showed that no reaction occurred between 1-methylcyclohexene and HCl under the experimental conditions. Since the only monochlorinated product was 1-chloro-1-methylcyclohexane (*i.e*, no 2-chloro-1-methylcyclohexane could be detected at low conversion), the addition of H atom appeared to take place at the secondary carbon of the double bond (eq 8, 9). Beside the expected products (chloroform, methylcyclohexane, methylenecyclohexane, 1-chloro-1-methylcyclohexane, hexachloroethane and dimeric compound 1,1'-dimethyl-1,1'-bicyclohexyl), an additional chlorine containing product, 7,7-dichloro-1-methylbicyclo-[4.1.0]heptane was formed, see Table III-3.

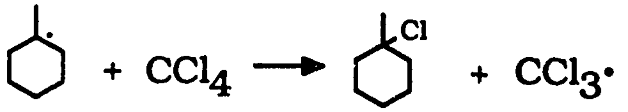


(8)

Table III-3. The Product Distribution from the Reaction of Atomic Hydrogen with 1-Methylcyclohexene in the Presence of Carbon tetrachloride (–78 °C)[a]

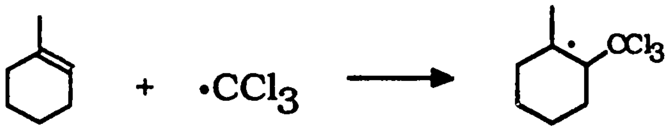
[CCl_4] (M)	CCl_4 conversion (mole × 10^{-4})	Product[b] (mole × 10^4)						
		$HCCl_3$				C_2Cl_6		
0.050	7.4	3.8	39.7	14.3	9.2	0.7	1.9	0.01
0.104	6.1	2.6	17.3	8.8	7.5	1.1	1.2	tr.
0.258	10.8	3.6	13.7	8.4	13.8	3.7	1.8	tr.
0.401	31.1	8.6	18.7	9.6	34.5	8.3	4.5	tr.

[a] The concentration of 1-methylcyclohexene is 1.060 M in acetone. [b] Trace of HCl was detected.



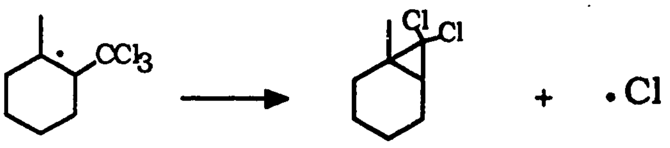
(9)

Since atomic hydrogen competitively adds to the olefinic double bond and abstracts from CCl_4, both products of the tertiary radical and the CCl_3• radical are predictably formed. The reaction of CCl_4 with the H atoms as well as the alkyl radical is established by the observation that the products from the intermediate CCl_3• radical, *i.e.* chloroform, hexachloroethane as well as the unexpected product, 7,7-dichloro-1-methylbicyclo[4.1.0]heptane, are produced. The formation of the bicyclic product appears to be the result of a radical displacement on carbon (eq 10, 11).



(10)

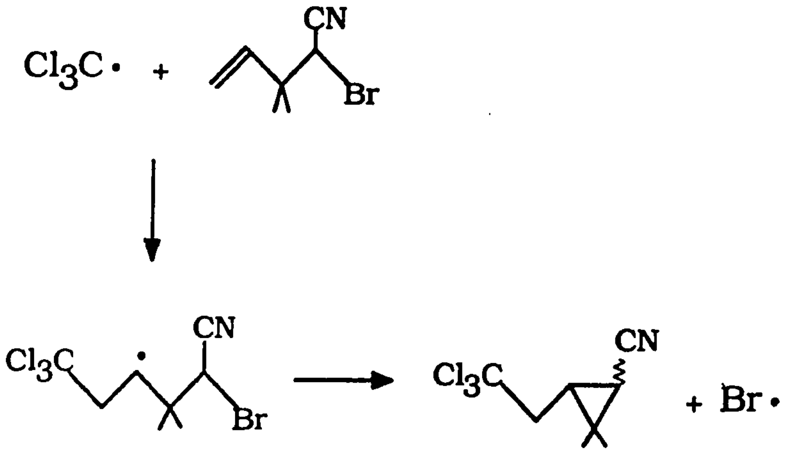
3b



(11)

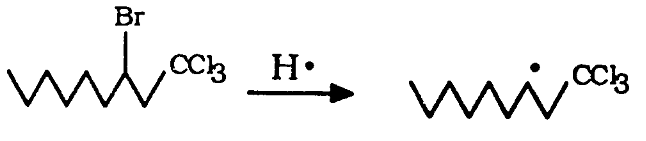
Although examples of S_H1 displacements on carbon are rare, they are not unprecedented. Johnson *et al*[2,3] reported that two isomeric 1-cyano-2,2-

dimethyl-3-(β,β,β-trichloroethyl)cyclopropanes were formed through a radical cyclization pathway from the reactions of 1-bromo-1-cyano-2,2-dimethylbut-3-ene with carbon tetrachloride, bromotrichloromethane or trichloromethanesulphonyl chloride (eq 12).



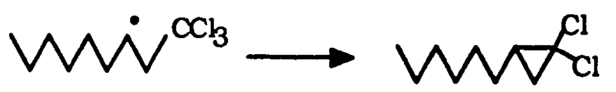
(12)

To test the hypothesis that the three member-ring system was formed via a radical displacement, 3-bromo-1,1,1-trichlorononane was synthesized and allowed to react with atomic hydrogen. As predicted, 1,1-dichloro-2-hexylcyclopropane resulting from the reactions of radical **3c** was formed although not as the exclusive product (eq 13, 14).



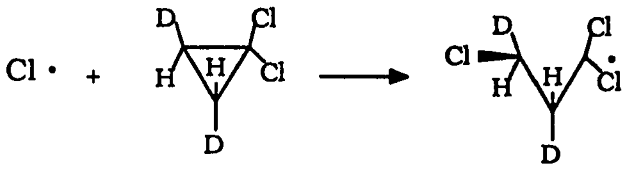
(13)

3c

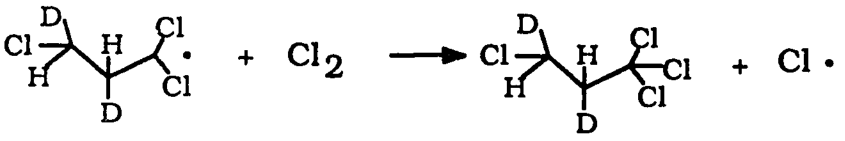


(14)

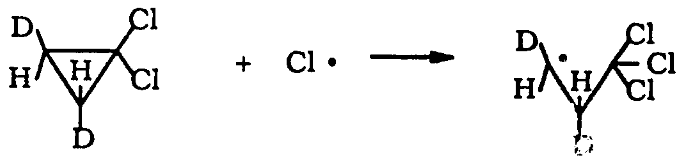
Other radical displacements on carbon which have previously been reported involve ring opening reactions of cyclopropane.[4] The classical chlorine atom promoted ring opening reactions of cyclopropane studied by Applequist,[4g] Walling,[5] and Incremona[6] are the most well documented of these displacements. A typical example reported by Incremona[6] was the ring opening reaction of 1,1-dichlorocyclopropane (eq 15, 16).



(15)

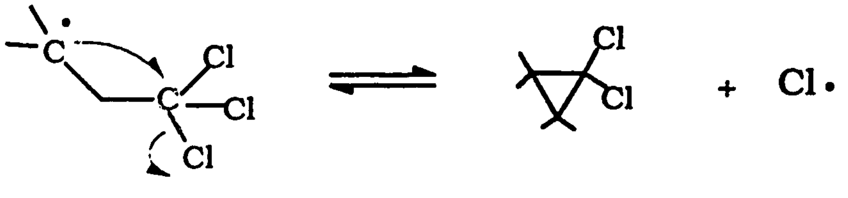


(16)



(17)

Stereospecific ring opening necessitates the attack on the carbon with no chlorine (eq 15). However, a portion of the reaction was not stereospecific and led to a nonstereospecific ring opening product presumably formed by chlorine atom attack at the dichlorinated carbon (eq 17). Although the reaction (17) is a minor pathway, it represents the reverse of the ring closure reaction (18). The ring opening of reaction (17) is promoted by the relief of cyclopropyl ring strain. Ring closure occurs to give a stable product if the β-radical undergoes bimolecular reaction slowly.


(18)

Since no 1,2-addition product, 1-chloro-1-methyl-2-(trichloromethyl)-cyclohexane, was detected in the product mixture, see Table III-3, the reaction was carried out at a high concentration of CCl_4 (4 M) in order to make 1,2-addition more favorable. However, even at high CCl_4 concentration, no 1,2-addition takes place, and at this temperature $k_t/k_c << 1$, where k_t is the transfer rate constant, and k_c is the cyclization rate constant.

At –78 °C, ring closure, k_c, takes place (eq 11) in preference to 1,2 addition, k_t, (eq 19). This observation is not surprising since the rate of transfer of the sterically hindered tertiary radical is expected to be very slow under the experimental conditions. The slow transfer rate can be explained from the following calculations: the Arrhenius equation $\log k_t = 8.1 - 5500/2.303RT$ was reported by Newcomb[8a] for the chlorine transfer of the primary radical with CCl_4. The transfer rate constants (k_t) at –78 °C, –42 °C, and 100 °C were calculated from this equation as 0.8×10^2, 7.7×10^2 and 7.8×10^4 $M^{-1}s^{-1}$, respectively, see Table III-4. Therefore, even using the primary radical as a model, the transfer rate at –78 °C is very slow. Table III-4 also lists the calculated transfer rate constants (k_t) at different temperatures for poly(methyl methacrylyl) radicals. The calculations are based on the chain transfer constants for CCl_4, k_t/k_p, and the propagation

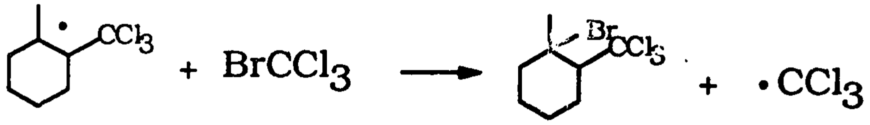
Table III-4. The Comparison of Transfer Rate Constants and Cyclization Rate Constants Using Different Radical Models

Model	Reactant	Donor	Temp. (°C)	E_a (kcal/mol)	k_t ($M^{-1}s^{-1}$)	k_c (s^{-1})	log k_t/k_c	ref
$RCH_2\cdot$	1-octene	CCl_4	100	5.5	7.8×10^4			8a
			–42		7.7×10^2			
			–78		0.8×10^2			
		$BrCCl_3$	70	1.9	2.4×10^8			
			–42		6.2×10^7			
			–78		2.9×10^7			
			–100		1.5×10^7			
			70	0.1		4.5×10^6	1.98	
			–42			2.5×10^6	1.39	
			–78			1.9×10^6	1.18	
			–100			2.0×10^6	0.82	
$\sim\sim CH_2\dot{C}HOAc$	1-methylcyclohexene	CCl_4	100	13.78	4.7×10^8			8b
			–42		5.1×10^3			
			–78		2.0×10^1			
		$BrCCl_3$	70	5.82	1.3×10^7			
			–78		2.0×10^4			
			–78			7.0×10^5	0.03	

rate constants (k_p) reported for the poly(methyl methacrylyl) radical.[8b] The rate constant, k_t, equals 20.0 $M^{-1}s^{-1}$ was obtained at −78 °C, see Appendix III-1, which further substantiates the proposal that the transfer rate was even lower for the secondary radical having a electron withdrawing group on the radical center. Another model was the secondary benzylic polystyrenyl radical for which both the chain transfer constants, k_t/k_p and the propagation rate constants (k_p) were reported at several temperatures. An even lower value, 0.017 M^{-1} s^{-1} at −78 °C, was obtained from the calculations,[7] see Appendix III-2.


(19)

When a more favorable halogen donor, bromotrichloromethane, was used as a transfer agent, 1,2-addition product, 1-bromo-1-methyl-2-(trichloromethyl)cyclohexane, was formed (eq 20). An estimate of the

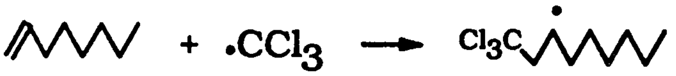

(20)

absolute rate constant for the cyclization, k_c, can be calculated using competition kinetics (eq 11, 20). The following relationship is obtained:

$$k_c = k_t [BrCCl_3] \frac{[P_c]}{[P_{12}]} \tag{21}$$

Where $[P_{12}]$ and $[P_c]$ are the concentrations of the 1,2-addition and cyclized product. Therefore, the absolute rate constant for cyclization at −78 °C, k_c equals 7.0×10^5 s^{-1}, can be estimated using the poly(methyl methacrylyl) radical as a model, see Table III-4.

The cyclization mechanism was further substantiated by carrying out the hydrogenation of 1-octene in the presence of each of the two transfer agents. The addition of the trichloromethyl radical to the terminal position of 1-octene yields a secondary alkyl radical **3c** (eq 22).



(22)

3c

Since the secondary alkyl radical **3c** is more reactive and less sterically crowded than the tertiary radical **3b**, a higher transfer rate is expected. Experimental results showed that no 1,2-addition product was detected when carbon tetrachloride (4 M) was used as transfer agent at temperatures of −78 °C and −42 °C. This result agreed with the low transfer rate constant calculated for primary and poly(methyl methacrylyl) radicals.

When bromotrichloromethane was used as the transfer agent for the reaction with 1-octene, higher ratios of $[P_{12}]$ /$[P_c]$ were obtained than those found for the reaction of 1-methylcyclohexene. The ratios of $[P_{12}]$/$[P_c]$ obtained from the analysis of the reaction mixture at −78 °C are listed in Table III-5. The absolute rate constant for the cyclization, k_c equals 1.9×10^6 s^{-1}, was calculated from eq 21, using the primary radical as a model, see

Table III-5. The Product Distribution of the Reaction of Atomic Hydrogen with 1-Octene in the Presence of Bromotrichloromethane (–78 °C)a

[BrCCl3] M	Products (mol × 10⁴)													
	$HCCl_3$				C_2Cl_6							others		 / 
0.25	0.5	33.2	8.1	1.8	14.6	25.7	0.5	0.1	8.6	0.1	0.9	3.2		8.2
0.80	7.5	23.3	5.0	0.8	39.8	74.5	2.4	0.9	3.2	0.3	14.1	7.4		15.2
1.65	16.6	71.2	7.7	1.4	81.7	83.1	3.3	2.6	5.5	0.6	62.2	10.6		24.4

a Reactions were carried out in neat 1-octene.

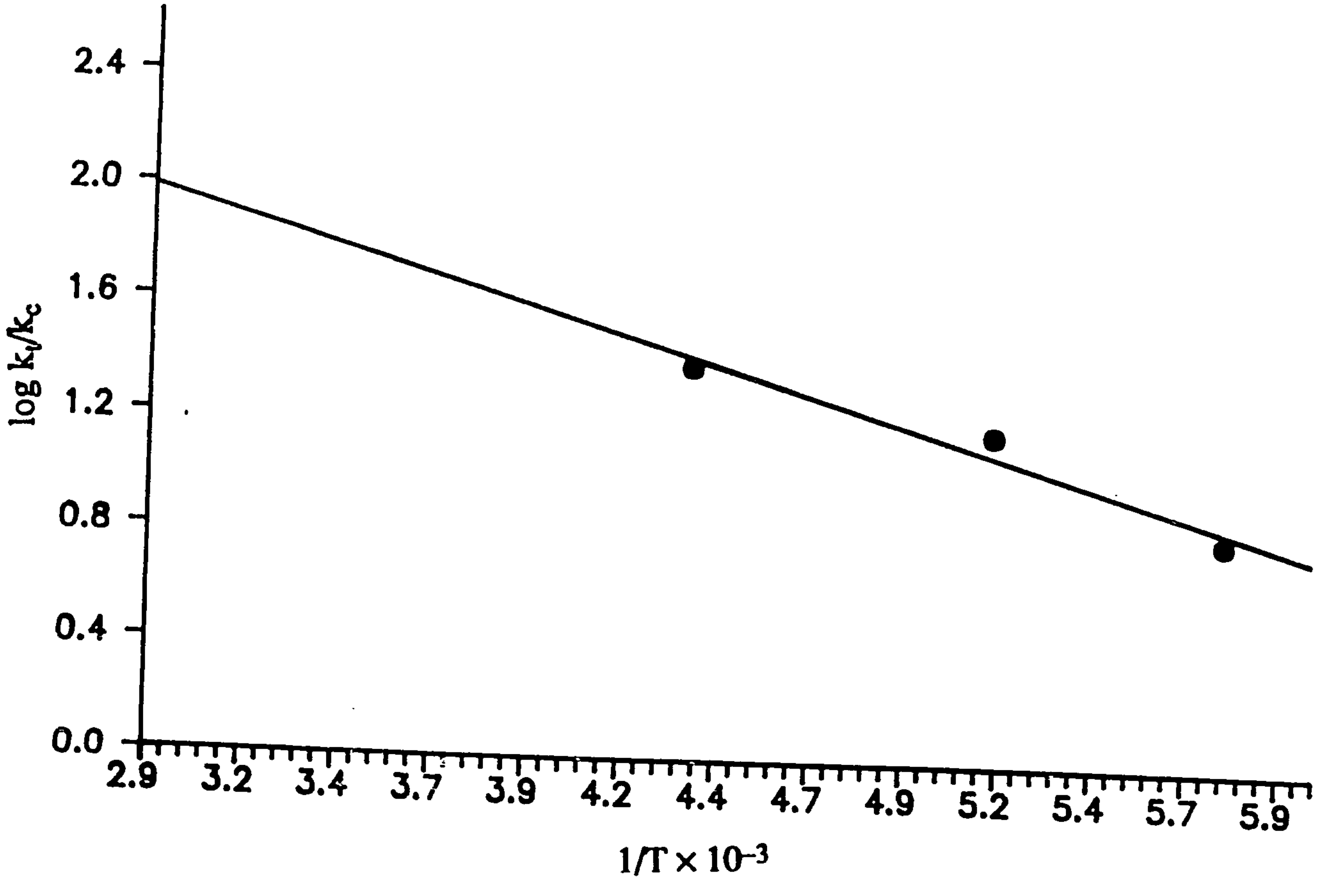


Fig. III-3. A plot of log k_t/k_c vs. $1/T$ for the reactions of *n*-hexyl-3,3,3-trichloropropyl radicals.

Table III-4. When reactions were carried out at –42 °C and –100 °C, rate constants, k_c equals 2.5 × 10^6 s^{-1} or 2.0 × 10^6 s^{-1}, were obtained, respectively. A plot of $\log(k_t/k_c)$ *vs.* 1/T gives a slope, $[E_{a(tr.)} - E_{a(cycl.)}]/2.303R$ equal to 0.39, see Fig. III-3. Since the activation energy $E_{a(tr.)}$ = 1.9 kcal mol^{-1}, the activation energy $E_{a(cycl.)}$ = 0.1 kcal mol^{-1} can be estimated using a primary radical as a model. The reaction temperature reported in the literature procedure for the synthetic preparation of 2-bromo-1,1,1-trichlorononane is >70 °C. The calculated rate constant, k_c = 4.5 × 10^6 s^{-1} at 70 °C, from the plot can be compared to the transfer rate constant k_t = 2.4 × 10^8 M^{-1} s^{-1} calculated at 70 °C, see Table III-4. This comparison predicts that the ratio of cyclization to 1,2-addtion product in neat bromotrichloromethane (10.16 M) is 1/542. Therefore, at this temperature the cyclization product is synthetically unimportant.

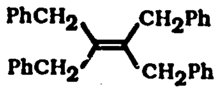
3. Allylic abstraction *vs.* addition

For small olefins in the gas phase near room temperature, abstraction of hydrogen from olefins by thermal hydrogen atoms is a relatively minor process compared with H atom addition.[9-14] Cvetanovic and coworkers[9,10] determined the ratio $k_{(H\ atom\ abstraction)}/k_{(H\ atom\ addition)}$ in the vapor phase to be 0.082, 0.093, 0.032, and 0.015 for propene, 1-butene, isobutene, and 1,3-butadiene, respectively. In these reports, the amount of abstraction never exceeded 10% of the total reaction at room temperature. The ratios of allylic abstraction relative to addition (room temperature) reported by Sunder[14] are even lower: propene, 0.2%; 1-butene, 1.6%; *cis*-2-butene, 1.5%; and *trans*-2-butene, 0.9%. On the basis of product analysis, we concluded that no allylic abstraction occurred during the H atom addition to 1-octene, *e.g.* $k_{(\text{H atom abstraction})} << k_{(\text{H atom addition})}$, see Chapter 2.

1-Octene, a monosubstituted ethylene, has two secondary C-H bonds. It was of interest to see if the competition of these two reactions could be made to favor allylic abstraction. Model olefins were used as substrates to make the addition more difficult due to steric hindrance, and make allylic abstraction more favorable by increasing the number of the allylic hydrogens. Since *trans*-2-octene, a disubstituted ethylene, has three primary and two secondary allylic C-H bonds, the reactions of H atoms with *trans*-2-octene were carried out at –78 °C, see Table III-6. GC/MS and GC/IR showed that no diolefinic monomer and unsaturated dimer were detected. The products are 1-octene (6.24%), *trans*-3-octene (1.20%), *cis*-3-octene (trace), octane (30.43%), *cis*-2-octene (6.47%), *meso*- and *d,l*-6,7-diethyldodecane (14.91%), *meso*- and *d,l*-6-ethyl-7-methyltridecane (28.02%), and *meso*- and *d,l*-7,8-dimethyltetradecane (12.72%). Since no diolefinic monomer and unsaturated dimer were formed from the disproportionation and combination of allylic radicals, no allylic abstraction occurred.

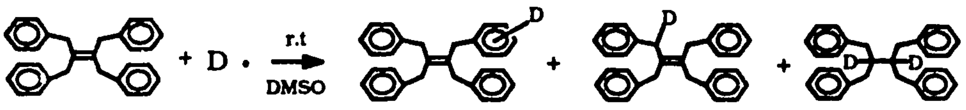
cis-3-Octene, a disubstituted ethylene, has four secondary allylic C-H bonds. The reaction of H atoms with *cis*-3-octene was carried out at –78 °C, and the product mixture was analyzed by GC/MS and GC/IR. No diolefinic monomers or unsaturated dimeric products were detected. The products are *trans*-3-octene, *trans*- and *cis*-4-octene, octane, *trans*-2-octene, *cis*-2-octene, 5,6-dipropyldecane, 6-ethyl-5-propylundecane, *meso- and d,l*-6,7-diethyldodecane. Since no diolefinic monomer and unsaturated dimer were formed from the disproportionation and combination of an allylic radical, no allylic abstraction occurred.

Table III-6. Allylic Abstraction vs. Addition for Reaction of the H Atom with Several Olefins

Olefin	Structure feature	Allylic abstraction
	monosubstituted ethylene secondary allylic C-H	no
	disubstituted ethylene primary & secondary allylic C-H	no
	disubstituted ethylene secondary allylic C-H	no
	tetrasubstituted ethylene primary allylic C-H	no
	tetrasubstituted ethylene benzylic C-H	yes

In the case of H atom addition to tetramethylethylene, a tetrasubstituted ethylene, the major product was 2,3-dimethylbutane, and only a trace of 2,3,3,4,4,5-hexamethylhexane were detected. Therefore addition was the only reaction which occurred.

In order to make abstraction compete with addition, tetrabenzylethylene, which has an extremely hindered double bond and eight benzylic C-H bonds available for hydrogen abstraction, was synthesized and used as a model for the reaction with atomic hydrogen (23 °C, DMSO). The mixture was analyzed by HPLC. No reduction products were detected, and only the starting material was recovered. In order to observe the hydrogen abstraction or the exchange of the hydrogen on the aromatic rings, the reaction was carried out using deuterium. Again, only the starting material was recovered. However, ^2H NMR spectrum of the reaction product shows that deuteriums were incorporated into the benzene rings (δ 7.3) and benzylic positions (δ 1.5), eq 23.



(23)

I II 0%

The ratio of I / II = 12 : 1 was obtained from the integration of ^2H NMR spectrum. In an attempt to get reduction products, the reactions were also carried out in Freon-11 at −100 °C and in Flurolube at 70 °C which were inert to atomic hydrogen and not evaporated at 3.00 torr. In both cases only the starting material was recovered.

Conclusions

Addition of atomic hydrogen to 1-methylcyclohexene is regiospecific (−78 °C), *i.e.* addition is exclusively at the secondary carbon. No allylic abstraction takes place. The additions of atomic hydrogen to 1-methylcyclohexene in the presence of carbon tetrachloride or bromotrichloromethane yields 7,7-dichloro-1-methylbicyclo[4.1.0]heptane by a radical cyclization. Ring closure, k_c, takes place (eq 11) in preference to 1,2-addition, k_t, (eq 19) and is attributed to the low entropy and low activation energy of the unimolecular reaction at low temperature. Similarly, the additions of atomic hydrogen to 1-octene in the presence of carbon tetrachloride or bromotrichloromethane yield 1,1-dichloro-2-hexylcyclopropane.

Only addition products are observed for the reactions of mono-, di-, tri-, and tetra-alkyl substituted olefins with atomic hydrogen. When atomic hydrogen adds to the extremely hindered olefin tetrabenzylethylene, only addition to the aromatic ring and abstraction from benzylic C-H were observed.

Experimental

1. Materials - 1-Methylcyclohexene (FLUKA, +99%), CCl_4 (HPLC grade, +99%), $BrCCl_3$ (Aldrich, spectrophotometric grade, +99.5%), *cis*-2-octene and *cis*-3-octene (Philiphs research grade, +99%), 2,3-dimethyl-2-butene (Aldrich, +99%), 2,3-dimethylbutane (Aldrich, +99%), and octane (Aldrich, +99%) were checked by GC prior to use.

7,7-Dichloro-1-methylbicyclo[4.1.0]heptane was prepared according to the literature procedure.[15] The product was isolated in 62% yield: ^1H NMR (400 MHz, $CDCl_3$): δ 1.18-1.42 (m, 8H), 1.64-1.72 (m, 2H), 1.79-1.98 (m, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): 73.18 (s, 1), 32.00 (d, 1), 27.27 (t, 1), 26.61 (s, 1), 25.54 (q, 1), 20.86, 20.13, 18.87 (t, 3). Anal. calcd for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75. Found: C, 53.75; H, 6.90.

3-Bromo-1,1,1-trichlorononane was prepared according to the literature procedure.[16] The product was obtained in 51% yield: bp 235 ^oC/701 mm Hg (lit.[16] 60-70 ^oC/0.3 mm Hg); ^1H NMR (200 MHz, $CDCl_3$): δ 0.85 (t, 3H, J = 7 Hz), 1.25-1.60 (m, 8H), 1.85-2.10 (m, 2H), 3.12-3.25 (dd, 1H, J = 4, 16 Hz), 3.35-3.50 (dd, 1H, J = 4, 16 Hz), 4.25-4.40 (m, 1H); IR (vapor) ν 2936, 2870, 1462, 1314, 1172, 1114, 1039, 953, 782, 707 (st, 1:1) and 630 cm^{-1}. The mass spectrum had a molecular ions at m/z = 308, 310, 312, 314 expected for $C_9H_{16}Cl_3Br$ and the isotope distribution matched the expected mass spectral cracking pattern.

Tetrabenzylethylene was prepared according to the literature procedure.[17] 1,3-Diphenylacetone (Aldrich) was reacted with anhydrous titanium trichloride and lithium in 1,2-dimethoxyethane. The resulting product was recrystallized from methanol and purified by flash chromatography to yield 73% of tetrabenzylethylene as a crystalline solid:

mp 121-122 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.61 (s, 8 H), 7.2-7.4 (m, 20 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 37.23, 126.13, 128.52, 128.71, 134.37, 140.35; IR 3030 (benzene ring CH), 1600 cm^{-1} (C=C). Anal. Calcd for $C_{30}H_{28}$: C, 92.74; H, 7.26. Found: C, 92.44; H, 7.26.

2. Methods and Procedures

GC analyses and spectral measurements were carried out using the instrumentation described in Chapter 2. Microanalyses were performed at the Microanalytical laboratory, Department of Chemistry, University of Alberta.

In all cases a capillary column Rtx-1 (105 m × 0.25 mm × 0.5 m, RESTEK corporation) was used for the quantitative GC analysis.

General Procedure for the Atomic Hydrogen Reaction. - An aliquot solution was placed in the U-shaped reactor. The reactor was cooled to –78 °C. Hydrogen [illegible] deuterium was passed into the system at a flow rate of 4 ml/min. The [illegible] system pressure was controlled at 3.00 torr by valve 1 (see Fig. II-4). The microwave generator output was adjusted to 80% and the reaction allowed to proceed. After the reaction, the product mixture was transferred into a vial and analyzed by GC. For each reaction, the products were identified by comparison of their GC retention times, GC/MS, and GC/IR with those of authentic samples.

General Procedure for Reactions with 1-Methylcyclohexene. Neat 1-methylcyclohexene was used, and the general procedure for the atomic hydrogen reaction was followed. The products were analyzed by GC and characterized by GC/IR and GC/MS. ^{2}H NMR spectra were obtained for products of the reactions with deuterium.

General Procedure for Reactions with 1-Methylcyclohexene and 1-Octene in the Presence of CCl_4 and $BrCCl_3$. An aliquot solution of olefin and $XCCl_3$ was used as substrate. The general procedure for the atomic hydrogen reaction was followed. The products were analyzed by GC and characterized by GC/IR and GC/MS.

The Reaction of Atomic Hydrogen with *trans*-2-Octene, *cis*-3-Octene and 2,3-Dimethylbutene. An aliquot solution of olefin (1 M in acetone) was used for the reaction. The general procedure for the atomic hydrogen reaction was followed. The products were analyzed by GC and characterized by GC/IR and GC/MS.

The Reaction of Atomic Hydrogen with Tetrabenzylethylene. A solution of tetrabenzylethylene (1 M in DMSO, Freon-11 or Flurolub) was used for the reactions. The general procedure for the atomic hydrogen reaction was followed. The products were analyzed both by TLC and by HPLC. HPLC analyses were carried out on a Perkin-Elmer Series 2 Liquid chromatograph with a Perkin-Elmer LC-55B Spectrophotometric Detector and Varian Vista CDS 401 chromatograph data system. An S_1-normal phase Radial-PAK Liquid Chromatography Cartridge column was used for the HPLC analysis. Hexane was used as eluant.

3. Identification of Products - Chloroform, methylcyclohexane, 1-octene, methylenecyclohexane, hexachloroethane, 1-bromooctane, 2-bromooctane, *trans*- and *cis*-2-octene, *trans*- and *cis*-3-octene, *trans*- and *cis*-4-octene, *n*-octane, and 2,3-dimethylbutane were identified by a comparison of their retention time on GC, GC/MS and GC/IR with those of authentic samples.

***dl-* and *meso*-7,8-Dimethyltetradecane** (1:1) **and 7-methylpentadecane** were identified by a comparison of their GC retention times, GC/IR and GC/MS with those of compounds identified in Chapter 2.

1-Chloro-1-methylcyclohexane was prepared according to the literature procedure.[18] A 250 ml flask, fitted with an inlet tube reaching to the bottom, a thermometer and an exit tube for conducting away excess gas, was immersed in an ice-water bath. The flask was charged with 1 g of pure methylcyclohexene, while temperature of the liquid was kept at 5-10 °C. Dry HCl was passed in at a moderate rate until the liquid was saturated with HCl. At this temperature addition took 8 hours. Distillation gave 1.1 g (81%) of 1-chloro-1-methylcyclohexane: bp 30-31 °C/6 mm Hg (lit.[19] bp 65.2-65.5 °C/ 44 mm Hg); ^{13}C NMR (300 MHz, $CDCl_3$) δ 23.89 (q, 1), 23.01, 25.23, 30.03, 41.58 (t, 5), 72.00 (s, 1); IR (gas phase): ν 2944, 2873, 1452, 1383, 1255, 1147, 982, 880, 777 and 682 cm^{-1}; EI^+ (GC/MS, VG-70) m/z: 132 (M^+, ^{35}Cl), 117, 97, 96, 81, 67, 55, and 41. 1-Chloro-1-methylcyclohexane in the product mixture was identified by comparison of its GC retention time, and GC/MS and GC/IR with the synthetic material.

1,1'-Dimethyl-1,1'-bicyclohexyl was isolated from the reaction product mixture of atomic hydrogen with 1-methylcyclohexene. The structure of the dimer was identified by an analysis of its GC/MS, GC/IR, ^1H NMR, ^{13}C NMR and APT: ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (s, 6H), 1.20-1.80 (m, 20H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 16.61 (q, 2), 30.34, 26.61, 30.34 (t, 5), 38.15 (s, 2); IR (gas phase): ν 2937, 2872, 1455, 1382, and 1302 cm^{-1}; EI^+ (GC/MS, VG-70) m/z: 194 (M^+), 97, 96, 81, 69, 68, 67, 55, 41.

1,1-Dichloro-2-hexylcyclopropane was prepared according to the literature procedure[13] and identified by its GC/MS, GC/IR, ^1H NMR, ^{13}C

NMR and APT: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H, J = 7 Hz), 1.35 (m, 1H), 1.25-1.40 and 1.42-1.60 (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.09 (q, 1), 22.64, 26.82, 28.61, 28.98, 30.41, 31.77 (t, 6), 30.97 (d, 1), 61.73 (s, 1); IR (gas phase): ν 2936, 2869, 1460, 1384, 1125, 1046, and 752 cm^{-1}; EI$^+$ (GC/MS, VG-70) m/z: 194, 196, 198 (M$^+$, $C_9H_{12}Cl_2$), 166, 152, 138, 123, 102, 83, 70, 56, and 41.

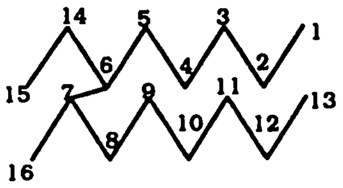
1-Chloro-1-methyl-2-(trichloromethyl)cyclohexane was prepared according to the literature procedure.[20] EI$^+$ (GC/MS, VG-70) m/z: 250 ($C_8H_{12}{}^{35}Cl_3{}^{37}Cl$), 248 ($C_8H_{12}{}^{35}Cl_3{}^{37}Cl$) 213, 175, 129, 109, 93, 77, 65, 53 and 41; IR (gas phase): ν 2931, 2875, 1454, 1388, 1261, 1125, 933, 781 (st), 658 and 585 cm^{-1}. 1-Chloro-1-methyl-2-(trichloromethyl)cyclohexane in the product mixture was identified by a comparison of its GC retention time and GC/IR and GC/MS with the above synthesized sample.

1-Bromo-1-methyl-2-(trichloromethyl)cyclohexane was prepared according to the literature procedure.[20] IR (gas phase): ν 2943, 2876, 1454, 1388, 1251, 1128, 929, 885, 777 (st) and 648 cm^{-1}. EI$^+$ (GC/MS, VG-70) m/z: 217, 215, 213 ($C_8H_{12}Cl_3$) 179, 177, 143, 141, 109, 105, 95, 55 and 41. 1-Bromo-1-methyl-2-(trichloromethyl)cyclohexane in the product mixture was identified by a comparison of its GC retention time and GC/IR and GC/MS with the above synthesized sample.

1,1,1,3-Tetrachlorononane was prepared according to the literature procedure,[20] and identified by its GC/MS, GC/IR, ^{1}H NMR, ^{13}C NMR and APT: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85-0.92 (t, 3H, J = 7 Hz), 1.25-1.60 (m, 6H), 1.75-1.95 (m, 2H), 3.08-3.17 (dd, 1H, J = 4, 15.5 Hz), 3.23-3.31 (dd, 1H, J = 6, 15.5 Hz), 4.20-4.30 (m, 1H); ^{13}C NMR and APT (300 MHz, $DCCl_3$): 14.09 (q, 1), 22.60, 26.02, 28.59, 31.67, 39.12 (t, 5), 62.37 (t, 1), 97.05 (s, 1), 57.79 (d, 1); IR (vapor) ν 2930, 2870, 1462, 1350, 1215, 1117, 1040, 950, 782, 708 (st, 0.8:1) and 579 cm^{-1}; EI$^+$ (GC/MS, VG-70) m/z: 222.8, 184.8, 157.0, 132.0, 108.9, 96.0, 70.0, 55.0, and 43.0.

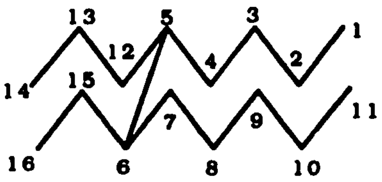
GC/IR and GC/MS were obtained for all of the dimeric products formed in the reaction of atomic hydrogen with *trans*-2-octene and *cis*-3-octene. GC/IR showed that all of dimers were saturated hydrocarbons, and the mass spectra of each had molecular ions at m/z = 226 as expected for $C_{16}H_{34}$.

dl- **and** ***meso*-6-Ethyl-7-methyltridecane** were obtained by preparative glpc collection (100 °C, 10 ft × 1/4 in. SE-30 column) of the product mixture resulting from the atomic hydrogen addition to *cis*-2-octene. A mixture of *dl-* and *meso*-6-ethyl-7-methyltridecane was obtained. GC and GC/MS showed two isomers in a 1:1 ratio: ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.76 (dd, 3H, J = 6.6 Hz), 0.88-0.92 (t, 9H, J = 6.6 Hz), 1.20-1.35 (m, 22H); ^{13}C NMR (300 MHz, DCCl$_3$): δ 12.68 and 12.44 (C_{15}, *meso-* and *dl-*), 15.55, 15.70(C_{16}, *meso-* and *dl-*), 14.12 (C_1 and C_{13}, *meso-* and *dl-*), 44.30, 41.31 (C_6 and C_7, *meso-* and *dl-*).

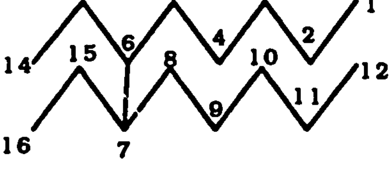


5,6-Dipropyldecane was obtained by preparative glpc collection (100 °C, 10 ft × 1/4 in. SE-30 column) of the product mixture resulting from the atomic hydrogen addition to *cis*-4-octene. ^{1}H NMR (300 MHz, CDCl$_3$): 0.85-0.92 (m, 12H), 1.18-1.32 (m, 22H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 14.21 (q, 2), 14.56, 21.26, 23.17, 30.08, 30.43, 33.19 (t, 10), 39.31 (d, 2).

6-Ethyl-5-propylundecane was obtained in a mixture with 5,6-dipropyldecane and *meso-* and *d,l*-6,7-diethyldodecane (in 3:2:1 ratio) by preparative glpc collection (100 °C, 10 ft × 1/4 in. SE-30 column) of the product mixture resulting from the atomic hydrogen addition to *cis*-3-octene. ^{1}H NMR (300 MHz, $CDCl_3$): 0.85-0.92 (m, 12H), 1.15-1.35 (m, 22H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.20 (C_1 and C_{11}), 14.54 (C_{14}), 12.73 (C_{16}), 38.95, 41.60 (C_5 and C_6).



d,l- **and** ***meso*****-6,7-Diethyldodecane** (1:1) was obtained in a mixture with *meso-* and *d,l*-6-ethyl-7-methyltridecane, and *meso-* and *d,l*-7,8-dimethyltetradecane (in 1:2:1 ratio) by preparative glpc collection (100 °C, 10 ft × 1/4 in. SE-30 column) of the product mixture resulting from the atomic hydrogen addition to *cis*-2-octene. GC and GC/MS showed two isomers in a 1:1 ratio: ^{1}H NMR (300 MHz, $CDCl_3$): 0.85-0.92 (m, 12H), 1.15-1.35 (m, 22H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.20 (C_1 and C_{12}, *meso-* and *dl-*), 12.72 (C_{14} and C_{16}, *meso-* and *dl-*), 41.30, 41.62 (C_6 and C_7, *meso-* and *dl-*).



2,3,3,4,4,5-Hexamethylhexane was obtained by preparative glpc collection (100 °C, 10 ft × 1/4 in. SE-30 column) of the product mixture resulting from the reaction of atomic hydrogen with 2,3-dimethylbutane. The structure was identified by its ^{1}H NMR and ^{13}C NMR. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (d, 12H, J = 7 Hz), 1.13 (s, 12H), 1.89-2.10 (m, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 17.47 (CH_3), 20.79 (CH_3), 33.87 (CH), 85.43 (C).

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CHAPTER 4

The Regioselective Reaction of Atomic Hydrogen with Unsymmetric Disulfides and Sulfides

*. A version of this chapter is in preparation for publication.

Introduction

In spite of the widespread interest in hydrogen atom chemistry, studies involving organosulfur compounds have been scarce. Some earlier kinetic studies dealt with the reactions involving H_2S and simple alkanethiols,[1] and interest in the biological effects of radiation led to studies of the reactions of atomic hydrogen with cysteine and cystine.[2,3] The necessity of removing the organosulfur compounds from crude oils directed attention to the reactions of hydrogen atoms with organo-sulfides, disulfides, and heterocyclic sulfur compounds. The gas phase reactions of atomic hydrogen with dimethyl disulfide,[4] diethyl disulfide,[5] ethyl methyl disulfide,[5] ditrifloromethyl disulfide,[6] and dibutyl disulfide[7] have been reported.

Reactions with disulfides

The Hg sensitized decomposition of H_2 in the presence of $C_2H_5SSC_2H_5$ yielded C_2H_5SH as the only retrievable product.[5] The principal elementary reaction between the H atom and the diethyl disulfide molecule was assumed to be a radical displacement reaction (eq 1).

$$H\cdot + C_2H_5SSC_2H_5 \rightarrow C_2H_5SH + C_2H_5S\cdot \qquad (1)$$

Kinetic determinations at various temperatures, in the presence of added ethylene, yielded an Arrhenius equation for reaction (1), relative to the known rate of addition of atomic hydrogen to ethylene.[5]

$$k = (4.73 \pm 0.64) \times 10^{13} \exp[(-1710 \pm 69)/RT] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The reaction of dibutyl disulfide with hydrogen atoms generated in a flow system by a microwave discharge at room temperature was studied by Amano and coworkers.[7] 1-Butanethiol, butane, and 1-butene were the main products. The reaction was carried out under pressures ranging from 133 to 2660 Pa. The following mechanism was proposed.

$$C_4H_9SSC_4H_9 + H\cdot \rightarrow n\text{-}C_4H_9SH + n\text{-}C_4H_9S\cdot \tag{2}$$

$$n\text{-}C_4H_9S\cdot + H\cdot \rightarrow n\text{-}C_4H_9SH^* + M \rightarrow n\text{-}C_4H_9SH \tag{3}$$

$$n\text{-}C_4H_9SH^* \rightarrow C_4H_8 + H_2S \tag{4}$$

$$n\text{-}C_4H_9SH^* \rightarrow n\text{-}C_4H_9\cdot + HS\cdot \tag{5}$$

$$n\text{-}C_4H_9\cdot + H\cdot \rightarrow n\text{-}C_4H_{10} \tag{6}$$

$$n\text{-}C_4H_9\cdot + H\cdot \rightarrow C_4H_8 + H_2 \tag{7}$$

Scheme IV-1.

H atom attack at one of the sulfur atoms was proposed to be the primary reaction. The intermediate radical formed subsequently decomposes to yield a thiol molecule and a thiyl radical. The secondary reaction of H· and dibutyl disulfide was the reaction of butylthiyl radical with a H atom to form activated butanethiol which can be collisionally deactivated to give thermalized thiol, since the H atom concentration was maintained at the level not less than the concentration of the substrate.[7] *n*-Butane and 1-butene were formed from the activated butanethiol, Scheme IV-1.

The reaction of ethyl methyl disulfide with atomic hydrogen was studied by Strausz and coworkers using the Hg sensitized decomposition of H_2.[5] It was proposed that the H atoms react via two parallel and competing steps (eq 8, 9).

$$H\cdot + CH_3SSC_2H_5 \rightarrow CH_3SH + C_2H_5S\cdot \qquad (8)$$

$$H\cdot + CH_3SSC_2H_5 \rightarrow C_2H_5SH + CH_3S\cdot \qquad (9)$$

The very high initial quantum yields obtained for the formation of CH_3SSCH_3 and $C_2H_5SSC_2H_5$ indicate that the thiyl radicals propagate a chain of radical exchange reactions forming the two symmetric disulfides.

$$CH_3S\cdot + CH_3SSC_2H_5 \rightarrow CH_3SSCH_3 + C_2H_5S\cdot \qquad (10)$$

$$C_2H_5S\cdot + CH_3SSC_2H_5 \rightarrow C_2H_5SSC_2H_5 + CH_3S\cdot \qquad (11)$$

$$C_2H_5S\cdot + CH_3SSCH_3 \rightarrow CH_3SSC_2H_5 + CH_3S\cdot \qquad (12)$$

$$CH_3S\cdot + C_2H_5SSC_2H_5 \rightarrow CH_3SSC_2H_5 + C_2H_5S\cdot \qquad (13)$$

Termination of the chain and the final fate of the thiyl radicals were postulated as both combination and disproportionation processes, eq 14-20, although the products of disproportionation were not detected.[5]

$$CH_3S\cdot + CH_3S\cdot \rightarrow CH_3SSCH_3 \qquad (14)$$

$$CH_3S\cdot + CH_3S\cdot \rightarrow CH_3SH + CH_2S \qquad (15)$$

$$C_2H_5S\cdot + C_2H_5S\cdot \rightarrow C_2H_5SSC_2H_5 \qquad (16)$$

$$C_2H_5S\cdot + C_2H_5S\cdot \rightarrow C_2H_5SH + CH_3CHS \qquad (17)$$

$$CH_3S\cdot + C_2H_5S\cdot \rightarrow CH_3SSC_2H_5 \qquad (18)$$

$$CH_3S\cdot + C_2H_5S\cdot \rightarrow CH_3SH + CH_3CHS \qquad (19)$$

$$CH_3S\cdot + C_2H_5S\cdot \rightarrow C_2H_5SH + CH_2S \qquad (20)$$

Thiyl radicals react considerably more slowly with disulfides than H atoms since the rate constant for reaction (1) is 2.6×10^9 l mol^{-1} s^{-1} and the rate constants for reaction (10), (11), (12), and (13) are 0.014, 0.0078, 0.031, 0.019×10^9 l mol^{-1} s^{-1} at 25 ^{o}C.[6]

B. Reaction with sulfides

Ekwenchi *et al.*[8] studied the vapor phase reaction of atomic hydrogen, generated by the Hg sensitized decomposition of H_2, with diethyl sulfide in the temperature range 298-461 K. The major products were ethanethiol, ethylene, ethane and *n*-butane. The product yields and their variations with substrate pressure and temperature could be fully explained by a mechanism which is shown in Scheme IV-2. This mechanism assumes that the hydrogen atom attacks exclusively at sulfur atom forming a radical intermediate, which subsequently decomposes to give alkanethiol and an alkyl radical.

$$H\cdot + C_2H_5SC_2H_5 \rightarrow C_2H_5\dot{S}HC_2H_5 \tag{17}$$

$$C_2H_5\dot{S}HC_2H_5 \rightarrow C_2H_5SH + C_2H_5\cdot \tag{18}$$

$$2C_2H_5\cdot \rightarrow C_2H_4 + C_2H_6 \tag{19}$$

$$2C_2H_5\cdot \rightarrow C_4H_{10} \tag{20}$$

$$C_2H_4 + H\cdot \rightarrow C_2H_5\cdot \tag{21}$$

Scheme IV-2 The mechanism for the reaction of diethyl sulfide with atomic hydrogen

The rate of the reaction of atomic hydrogen with diethyl disulfide ($k = (4.7 \pm 0.9) \times 10^{13} \exp[(-3797 \pm 152)/RT]$ cm^3 mol^{-1} s^{-1}) was determined from a plot of the relative rate of the displacement reaction vs. the previously determined rate of addition to ethylene.[5]

Results and Discussion

1. The reaction of atomic hydrogen with disulfides

The reaction of an acetone solution of dibutyl disulfide with atomic hydrogen generated in a microwave discharge of H_2 yields 1-butanethiol as the only retrievable product. This result agrees with the reaction mechanism proposed by Strausz[5] which postulates that the principal elementary reaction between the H atoms and the dibutyl disulfide molecule is the radical displacement reaction, eq 22.

$$H\cdot + C_4H_9SSC_4H_9 \rightarrow C_4H_9SH + C_4H_9S\cdot \qquad (22)$$

The regioselective cleavage of an unsymmetric disulfide bond was investigated by allowing several unsymmetrically substituted disulfides to undergo reactions with atomic hydrogen. In order to test substituent steric effects, butyl *t*-butyl disulfide, *sec*-butyl *tert*-butyl disulfide, and *sec*-butyl hexyl disulfide were selected as model unsymmetric disulfides, see Table IV-1. Thiols and disulfides were products of the reactions. The observation that the ratios of product thiol, 1-butanethiol to *tert*-butanethiol, *sec*-butanethiol to *tert*-butanethiol, and 1-hexanethiol to *sec*-butanethiol were 2.16, 1.34, 1.28 respectively, suggest that the displacement on sulfur with the primary substituent is favored over that with a secondary or tertiary substituent which is no doubt a reflection of a steric effect.

The mechanism for the reaction of a disulfide with atomic hydrogen can be rationalized by displacement on sulfur either by direct displacement or by α-scission of the intermediate radical formed by addition of a

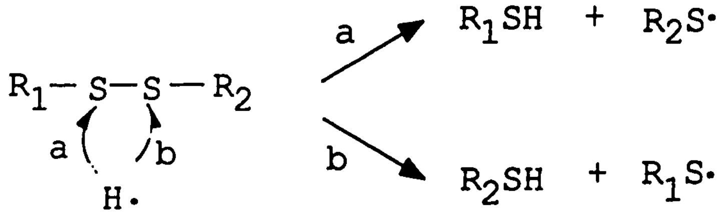
Table IV-1. The Product Distributions from the Reactions of Several Disulfides with Atomic Hydrogen[a]

	Starting Material	Conversion	Products (mol%)				R_1SH/R_2SH[b]
R_x	R_1SSR_2	(%)	R_1SH	R_2SH	R_1SSR_1	R_2SSR_2	
1	R_1= *n*-C_4H_9 R_2= *tert*-C_4H_9	5.7	51.6	24.1	5.4	18.9	2.16
2	R_1= *sec*-C_4H_9 R_2= *tert*-C_4H_9	4.3	43.8	33.2	6.9	16.1	1.34
3	R_1= *n*-C_6H_{13} R_2= *sec*-C_4H_9	3.4	42.7	33.4	9.9	14.0	1.28

[a] **Substrate concentration 0.05 M in acetone, reaction temperature –78 °C, pressure 3.00 torr, H_2 flow rate 0.5 mL/min.**

[b] **Ratio obtained from the extrapolation when $[R_1SSR_2] \rightarrow 0$ in Fig. IV-1, Fig. IV-2, and Fig. IV-3.**

hydrogen atom to one of the sulfur atoms (eq 23). Two thiols and two thiyl radicals were formed by either path a or path b.



(23)

The fate of the thiyl radicals is either to dimerize or to undergo radical exchange reactions with starting material to form the two symmetric disulfides, eq 26-30.

$R_1SSR_2 + H\cdot \rightarrow R_1SH + R_2S\cdot$ k_1 (24)

$R_1SSR_2 + H\cdot \rightarrow R_2SH + R_1S\cdot$ k_2 (25)

$R_1S\cdot + R_2S\cdot \rightarrow R_1SSR_2$ k_3 (26)

$R_1S\cdot + R_1S\cdot \rightarrow R_1SSR_1$ k_4 (27)

$R_2S\cdot + R_2S\cdot \rightarrow R_2SSR_2$ k_5 (28)

$R_1S\cdot + R_1SSR_2 \rightarrow R_1SSR_1 + R_2S\cdot$ k_6 (29)

$R_2S\cdot + R_1SSR_2 \rightarrow R_2SSR_2 + R_1S\cdot$ k_7 (30)

$R_1S\cdot + H\cdot \rightarrow R_1SH$ k_8 (31)

$R_2S\cdot + H\cdot \rightarrow R_2S\,H$ k_9 (32)

From equations 26-29, the following relationships were obtained:

$$d[R_1SSR_1]/dt = k_4\,[R_1S\cdot]^2 + k_6[R_1S\cdot]\,[R_1SSR_2] \qquad (33)$$

$$d[R_2SSR_2]/dt = k_5 [R_2S\bullet]^2 + k_7[R_2S\bullet] [R_1SSR_2] \qquad (34)$$

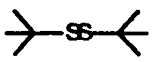
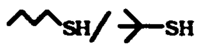
If radical displacement reactions contributed to the formation of symmetrical disulfides, the amount of symmetrical disulfides formed would be dependent on the concentration of R_1SSR_2. Different concentrations of butyl *t*-butyl disulfide were subjected to hydrogen atoms at very low flow rate (0.5 mL/min). The results are given in Table IV-2. The yield of symmetrical disulfides, 25.4±0.5, does not change as the concentration of the starting material increases. When $[R_1SSR_2] \rightarrow 0$, and $[H\bullet] \rightarrow 0$, equations 29 to 32 are not involved, since the ratios of $[R_1SH]/[R_2SH]$ extend to the same point, see Fig. IV-1. At this point, the formation of the symmetrical disulfides can only be ascribed to radical combination reactions, and the following equation should apply:

$$[R_1SH]/[R_2SH] = \{[R_2SSR_2] + [R_1SSR_2]_x\}/ \{[R_1SSR_1] + [R_1SSR_2]_x\} \qquad (35)$$

where $[R_1SSR_2]_x$ is the concentration of the combination product of unlike thiyl radicals. The product distribution in Table IV-2 agrees with such a relationship.

In a similar manner, different concentrations of *sec*-butyl *t*-butyl disulfide and *sec*-butyl hexyl disulfide were allowed to react with hydrogen atoms at a hydrogen flow rate of 0.5 mL/min. The results are given in Table IV-3 and IV-4, and in both cases the results were in agreement with the above relationship. However, the formation of thiol can be ascribed to the reaction of atomic hydrogen with the starting disulfide and the

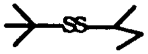
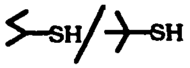
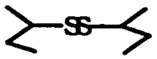
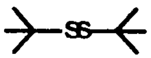
Table IV-2. The Product Distribution from the Reaction of Butyl *tert*-Butyl Disulfide with Atomic Hydrogen[a]

		Product (mol%)					
Concentration (M)	Conversion (%)					Total of symmetric disulfides[b]	
0.0466	13.8	51.6	24.1	18.9	5.4	24.3±1.1	2.14
0.1079	12.5	50.9	23.4	17.5	8.2	25.7±0.3	2.17
0.2427	6.9	51.7	22.1	17.2	9.0	26.1±0.8	2.33
0.4219	5.7	50.7	23.8	17.3	8.1	25.4±0.1	2.09
						25.4±0.6[b]	

[a] Solution in acetone, reaction temperature –78 °C, pressure 3.00 torr, H_2 flow rate 0.5 mL/min.

[b] Deviations from the average value.

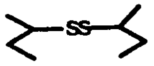
Table IV-3. The Product Distribution from the Reaction of *sec*-Butyl *tert*-Butyl Disulfide with Atomic Hydrogen[a]

Concentration (M)	 left (%)	Product (mol%)				Total of [b] symmetric disufides	
							
0.019	92.3	45.4	33.9	6.5	14.2	20.7±1.1	1.34
0.050	95.7	43.8	33.2	6.9	16.1	23.0±1.3	1.32
0.080	97.0	44.6	33.5	5.9	16.0	21.9±0.2	1.33
0.178	97.9	45.5	34.7	5.7	14.0	19.8±2.0	1.31
0.647	99.0	43.6	33.0	6.9	16.4	23.3±1.5	1.32
						21.7±1.2 [b]	

[a] Solution in acetone, reaction temperature –78 °C, pressure 3.00 torr, H_2 flow rate 0.5 mL/min.

[b] Deviations from the average value.

Table IV-4. The Product Distribution from the Reaction of *sec*-Butyl Hexyl Disulfide with Atomic Hydrogen[a]

Concentration (M)	Conversion (%)	Product(mol%)				Total of symmetric disulfide [b]	
							
0.023	4.5	42.1	32.9	14.2	10.8	25.0±0.6	1.28
0.056	3.4	42.7	33.4	14.0	9.8	23.9±0.4	1.28
0.110	3.2	43.6	33.8	12.9	9.6	22.6±1.7	1.29
0.297	3.0	42.6	32.7	14.2	10.5	24.7±0.4	1.30
0.478	2.1	42.0	32.5	14.3	11.2	25.5±1.1	1.29
						24.3±0.9 [b]	

[a] Solution in acetone, reaction temperature –78 °C, pressure 3.00 torr, H_2 flow rate 0.5 mL/min.

[b] Deviations from the average value.

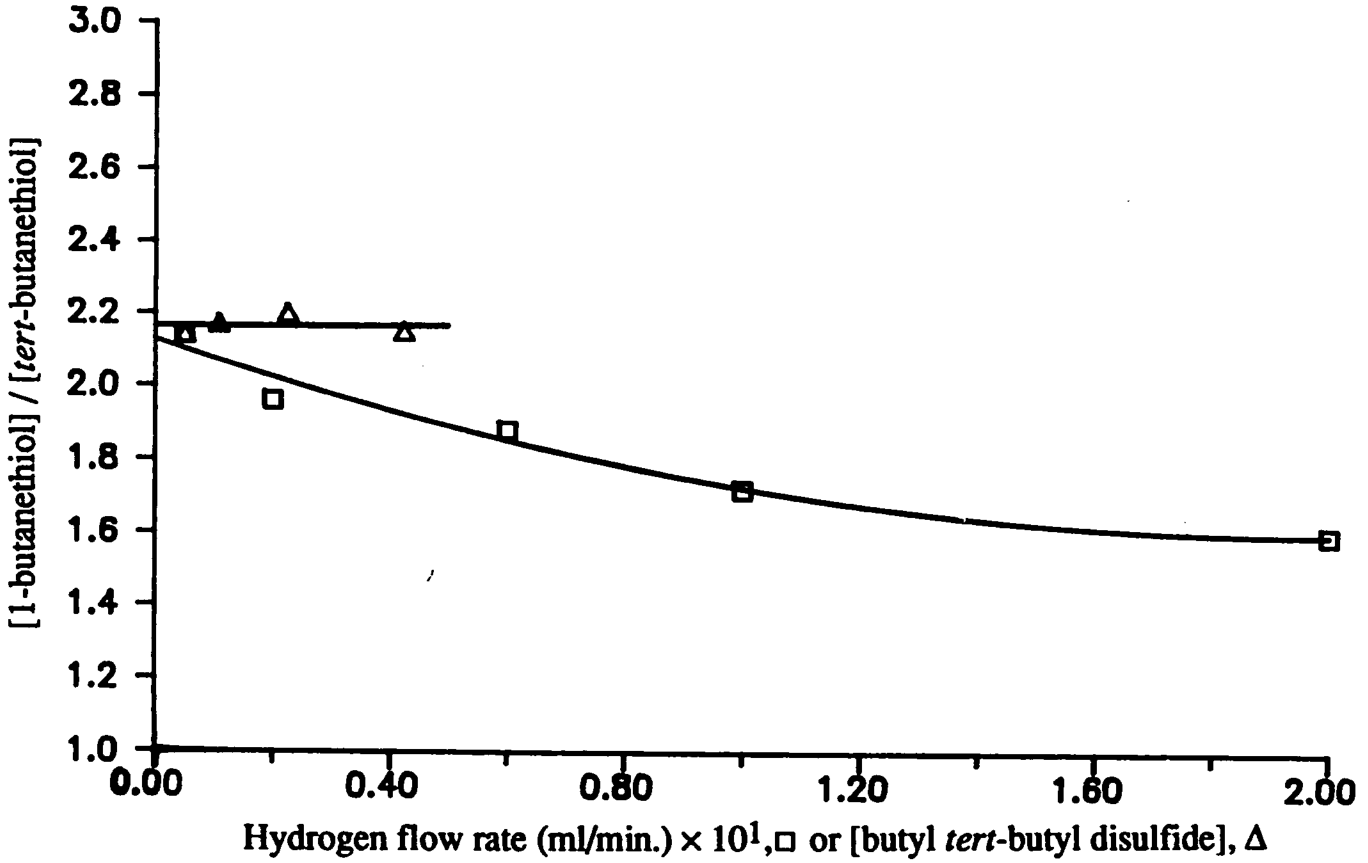


Fig. IV-1. A plot of the hydrogen flow rate and the concentration of Butyl *tert*-Butyl Disulfide *vs.* the ratio of [1-butanethiol]/[*tert*-butanethiol].

combination of atomic hydrogen with a thiyl radical. From equations 24-25 and equations 31-32, the rates of formation of the thiols can be expressed as

$$d[R_1SH]/dt = k_1\ [H\bullet]\ [R_1SSR_2] + k_8\ [H\bullet]\ [R_1S\bullet] \qquad (36)$$

$$d[R_2SH]/dt = k_2\ [H\bullet]\ [R_1SSR_2] + k_9\ [H\bullet]\ [R_2S\bullet] \qquad (37)$$

When the hydrogen flow rate is extrapolated to zero, *e.g.* $[H\bullet] \rightarrow 0$, reactions 31 and 32 can be neglected, and the following relationship is derived.

$$[R_1SH]/[R_2SH] = k_1 / k_2 \qquad (38)$$

The ratio of the two thiols should reflect the ratio of two reaction rates at zero hydrogen flow rate, see Fig.IV-1, Fig.IV-2, Fig.IV-3. The regioselectivity of attack at sulfur is calculated from the ratio of the two thiols. The calculated results are listed in Table IV-5. The ratio of thiols listed appears to result from the energy differences impressed by the bulk of the alkyl substitutent.

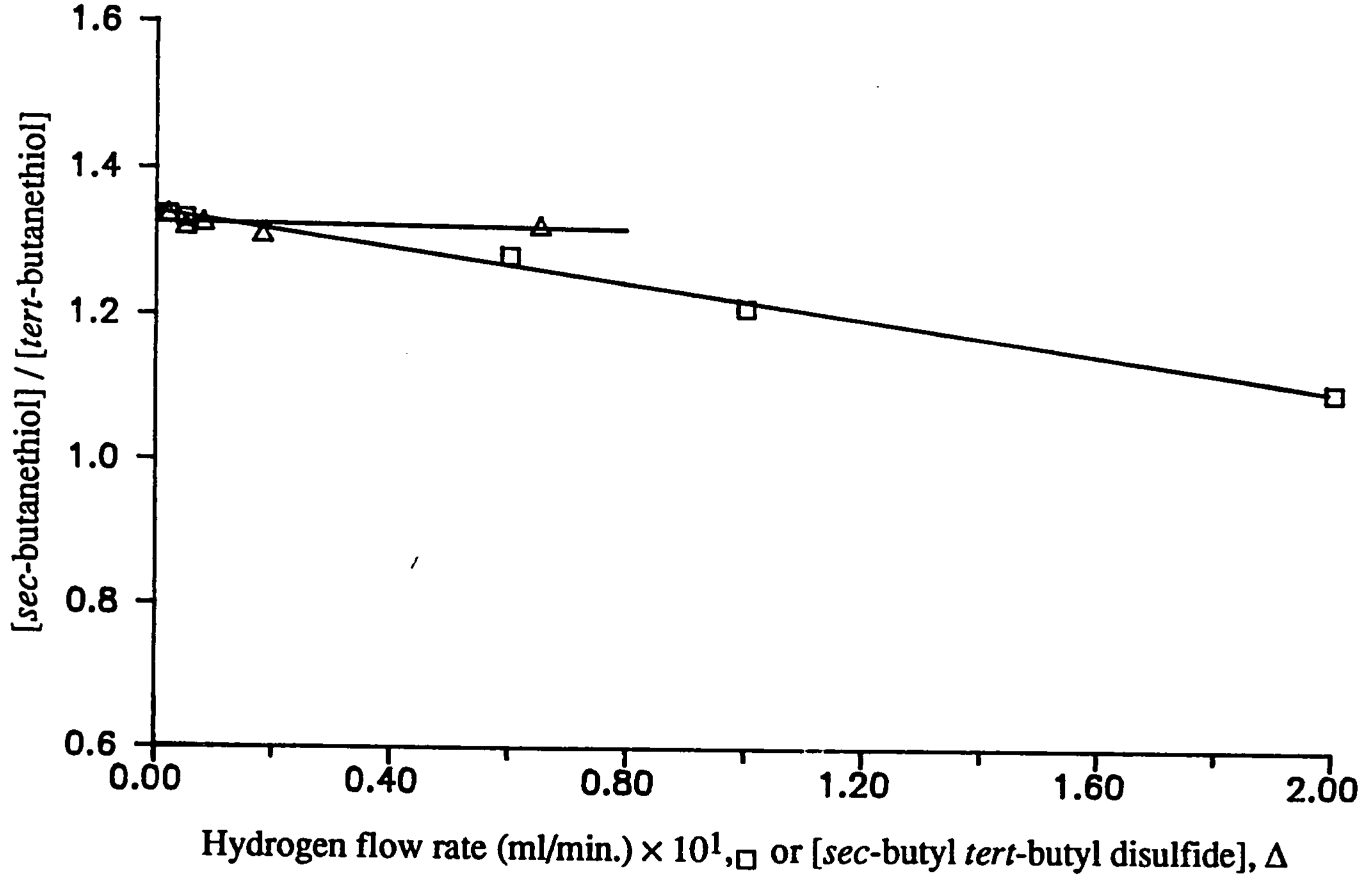


Fig. IV-2. A plot of the hydrogen flow rate and the concentration of *sec*-Butyl *tert*-Butyl Disulfide *vs.* the ratio of [*sec*-butanethiol]/[*tert*-butanethiol].

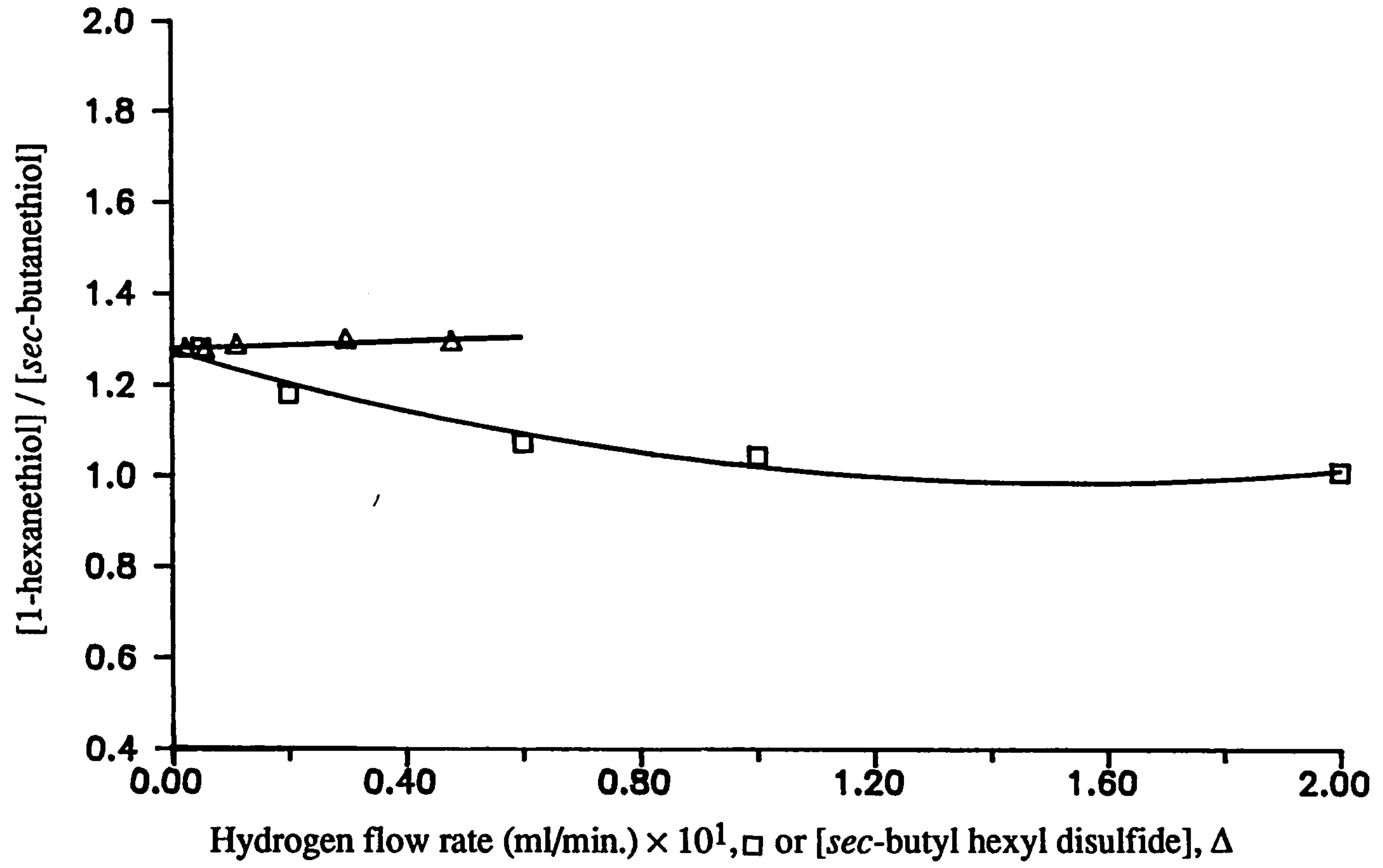


Fig. IV-3. A plot of the hydrogen flow rate and the concentration of *sec*-Butyl Hexyl Disulfide *vs.* the ratio of [hexanethiol]/[*sec*-butanethiol].

Table IV-5. The Regioselectivities of the Reactions of Atomic Hydrogen with the Unsymmetric Disulfides[a]

R_x (Table)	$[R_1SH]/[R_2SH]$ [b]	a(%) : b(%) [c]	R_1/R_2
(IV-1)	2.16	68 : 32	1° / 3°
(IV-2)	1.34	57 : 43	2° / 3°
(IV-3)	1.28	56 : 44	1° / 2°

[a] Acetone solution of substrate, –78 °C.

[b] The ratio of thiols obtained from the plots, Figs IV-1, 2, 3 at zero $[R_1SSR_2]$ or [H•].

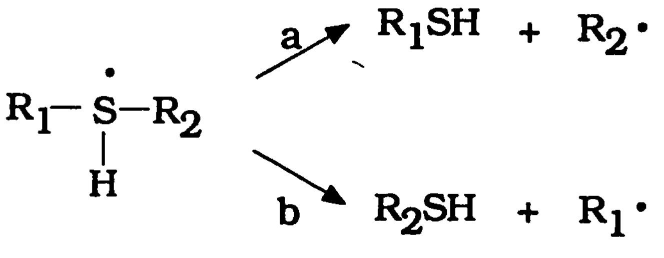
[c] % of attack by path a or b (eq 23).

The ratio of thiols is dependent upon the hydrogen flow rate, see Figs. IV-1, IV-2, and IV-3. This dependence can be interpreted as being due to the reaction of a thiyl radical with atomic or molecular hydrogen. Although bimolecular radical radical reactions even at diffusion controlled rates are quite unfavorable (eq 31, 32), the reaction of a thiyl radical with molecular hydrogen (eq 39) is extremely unattractive since its activation energy must be endoergonic by a minimum amount of 16 kcal/mol ($BDE_{(RS\text{-}H)}$ = 88 kcal/mol, $BDE_{(H\text{-}H)}$ = 104 kcal/mol).

$$RS\bullet + H_2 \rightarrow RSH + H\bullet \qquad (39)$$

2. The reaction of atomic hydrogen with sulfides

In order to investigate the selectivity of the cleavage of the sulfide bond, three unsymmetric compounds, *tert*-butyl hexyl sulfide, *tert*-butyl 2-octyl sulfide and *sec*-butyl hexyl sulfide, were selected as substrates for the reactions with atomic hydrogen. The results of these hydrogenolysis reactions are listed in Table IV-6. Displacement on sulfur is observed since the formation of the products are derived from the fragmentation of the alkyl-sulfur bond. When atomic hydrogen was passed over an acetone solution of *tert*-butyl hexyl sulfide (0.5 M) the products of the reaction were: isobutane, hexane, *tert*-butanethiol, 1-hexanethiol, *tert*-butyl hexyl disulfide, and dihexyl disulfide, see Table IV-6. The following mechanism can be proposed for the reaction of atomic hydrogen with a sulfide. The hydrogen atom adds to the sulfide and forms an intermediate RSHR•. Cleavage of the intermediate gives alkanethiol and an alkyl radical (eq 40). The two thiols and two alkyl radicals are formed by path a and path b.



(40)

The fate of the alkyl radicals is either to abstract a hydrogen atom from thiol or undergo disproportionation-combination reactions. However, alkanes were the only reduction products formed from the reaction of the alkyl radicals. This observation suggests that the radicals formed in the first step

Table IV-6. The Distribution of Products from the Reactions of Several Sulfides with Atomic Hydrogen (–78 °C)[a]

R_x	Starting Material R_1SR_2	Time (min.)	Conversion %	Products (mol%)						
				R_1H	R_2H	R_2SH	R_1SH	R_1SSR_2	R_1SSR_1	R_2SSR_2
1	R_1= *tert*-C_4H_9 R_2= *n*-C_6H_{13}	4	11.5	49.6	1.7	40.7	2.5	0.7	0	4.9
2	R_1= *tert*-C_4H_9 R_2= *sec*-C_8H_{17}	7	27.0	61.2	7.9	45.8	5.2	0.4	0	6.4
3	R_1= *sec*-C_4H_9 R_2= *n*-C_6H_{13}	6	21.4	43.1	3.0	33.1	9.5	3.6	0	7.7
4[b]	R_1= C_6H_5 R_2= *c*-C_6H_{11}	3	8.9	9.0	46.9[c]	4.0	37.5	0	2.2	0

[a] 0.5 M in acetone, Hydrogen flow rate 4 mL/min. [b] 0.1 M in acetone. [c] trace of cyclohexene found in the product.

will abstract a hydrogen from thiols (bond dissociation energy of CH_3S-H is 88 kcal/mol[11]), eq 41, 42. The rate constants for reactions of primary alkyl radicals with *tert*-BuSH have been reported as approximately 10^6 l mol^{-1} sec^{-1}.[12] Although disproportionation and combination reactions of alkyl radicals are diffusion-controlled, neither disproportionation nor combination products from the alkyl radicals could be detected. The thiyl radicals formed in this step either dimerize to give disulfides or react with a H atom to regenerate thiols. Since disulfide is only a minor product, the reaction with atomic hydrogen must dominant, see Appendix II-1B.

$$R_1SH + R_2\cdot \rightarrow R_2H + R_1S\cdot \qquad (41)$$

$$R_2SH + R_1\cdot \rightarrow R_1H + R_2S\cdot \qquad (42)$$

Table IV-6. shows that the major products of reaction 1 were isobutane and 1-hexanethiol derived from the cleavage of the *tert*-butyl-sulfur bond. Cleavage of the intermediate favors, as expected, the most stable radical. The selectivity of the displacement can be calculated from the ratio of sulfur containing compounds, in the product mixture, see Table IV-7. The ratio of a% : b% = 6.0 : 94.0 was obtained for the reaction of *tert*-butyl hexyl sulfide.

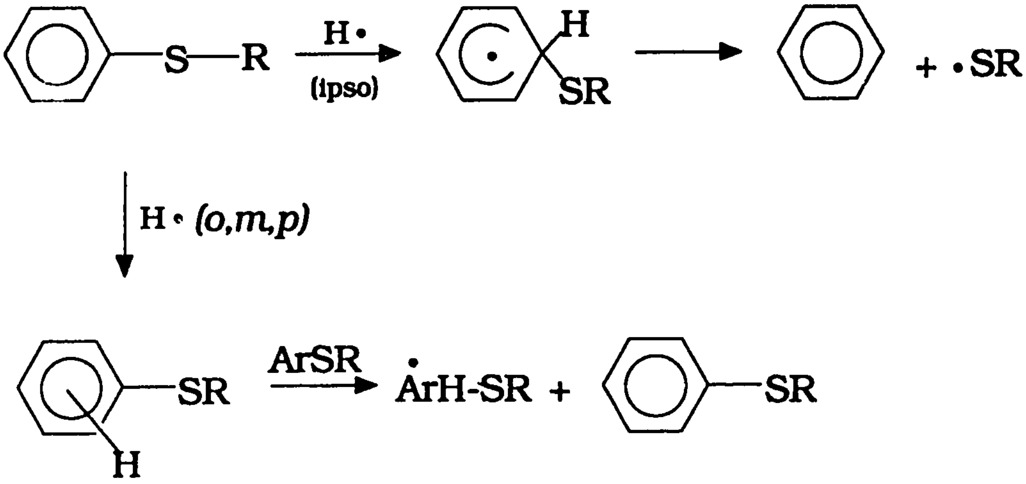
Table IV-7. The Selectivities of the Atomic Hydrogen Displacement on Sulfur

R_x	R_1S-/R_2S-	a(%) : b(%)	R_1/R_2
1	3.3/51.1	6.0 : 94.0	1°/3°
2	5.6/59.0	8.7 : 91.3	2°/3°
3	13.1/52.0	20.1 : 79.9	1°/2°

The hydrogenolysis of *tert*-butyl 2-octyl sulfide resulted in the formation of thiols, disulfide and hydrocarbons by the same mechanism, see Table IV-6. The selectivity of the displacement, a% : b% = 8.7 : 91.3, also reflects the relative stability of secondary and tertiary radicals.

When *sec*-butyl hexyl sulfide was used as a substrate (reaction 3), butane and 1-hexanethiol were the major products derived from the *sec*-butyl-sulfur bond cleavage. The ratio of a% : b% = 20.1 : 79.9 obtained agreed with the cleavage of the intermediate radical to give, as expected, the most stable alkyl radical, *e.g.* the *sec*-butyl radical.

In order to substantiate the above mechanism, the reaction of atomic hydrogen with cyclohexyl phenyl sulfide was carried out, see Table IV-6. Presumably, it is expected that no benzene would be formed. Benzene, however, was found in the product mixture. The formation of benzene and cyclohexanethiol derived from the fragmentation of the phenyl-sulfur bond in reaction 4 at first appears to be unlikely, however, the strength of the phenyl-sulfur bond in the intermediate is not known. Another cleavage mechanism resulting from *ipso*-attack followed by α-scission is a more attractive pathway which leads to the formation of benzene. To determine if the phenyl radical was formed from *ipso*-attack, cyclohexyl phenyl sulfide was allowed to react with atomic deuterium. A mass spectrum of the product, benzene, showed that one to two and possibly three deuteriums had been incorporated in the aryl ring at relatively low conversion (13.8%). The starting material had also incorporated deuterium. A mechanism which is consistent with these results is shown in Scheme IV-4. The H atom adds reversibly to the ring in the *o*-, *m*-, and *p*-positions. However, when the addition is to the *ipso* position, fragmentation occurs. The reversible transfer of a hydrogen atom from a cyclohexadienyl radical to an acceptor can leave deuterium in the aromatic ring. The deuterium isotope effect favors the transfer of protium.



Scheme IV-4

Conclusions

The reaction of atomic hydrogen with an unsymmetric disulfide is regioselective, *i.e.* addition at the least hindered sulfur atom is favored. The cleavage of the sulfur-sulfur bond of the intermediate formed by the addition gives a thiol and a thiyl radical. Symmetric disulfides in the product mixture were formed from the combination of thiyl radicals.

The addition of atomic hydrogen to an unsymmetric sulfide forms a metastable radical intermediate. Cleavage of the intermediate favors formation of the most stable radical, *i.e.* tertiary > secondary > primary.

The formation of benzene and cyclohexyl thiyl radical derived from the fragmentation of the phenyl-sulfur bond in the reaction of atomic hydrogen with cyclohexyl phenyl sulfide results from *ipso*-attack of atomic hydrogen to the benzene ring followed by α-scission.

Experimental

1. Materials - Dibutyl disulfide (98+%) , **dihexyl sulfide** (95+%), **1-butanethiol** (99+%), ***sec*-butanethiol** (98+%), ***tert*-butanethiol** (99+%), **cyclohexanethiol** (97+%), and **thiophenol** (99+%) were obtained from Aldrich, checked for purity by GC and used as received.

Butyl *tert*-butyl disulfide was prepared according to the literature procedure.[9] A solution of freshly distilled 1-bromobutane (137 g, 1.00 mol) in 1.2 L of methanol-water was heated to reflux, and sodium thiosulfate pentahydrate in 250 mL water was slowly added, the mixture was heated for 4 hours. After evaporating the methanol, the solution was diluted to 1.2 L and extracted twice with hexane. The aqueous solution of crude thiosulfate was cooled to 0 °C. In another flask, *tert*-butanethiol (90 g, 1.00 mol) was slowly added to 100 mL of NaOH (40 g, 1.0 mol) solution at room temperature with rapid stirring. The viscous solution was diluted with 30 mL of water and cooled to 0 °C. This thiolate solution was added rapidly to the previously prepared thiosulfate solution with vigorous stirring for 3 minutes. This was followed with addition of 200 mL of brine solution. The mixture was warmed to 5 °C. The crude disulfide which separated as an oil was washed, dried and filtered. Distillation of this crude material gave 50 g (28%) of pure disulfide: bp 196-198 °C; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.26 (s, 9H), 1.32 (m, 2H), 1.55 (m, 2H), 2.67 (t, 2H, J = 7 Hz); EI$^+$ (GC/MS, VG-70) m/z: 178 (M$^+$), 122, 87, 79, and 57; IR (vapor phase) ν 2969, 1464, 1367, 1275, 1168 and 746 cm^{-1}. Anal. Calcd for $C_8H_{18}S_2$: C, 53.87; H, 10.17; S, 35.95. Found: C, 53.98; H, 10.39; S, 35.60.

***sec*-Butyl *tert*-butyl disulfide** was prepared according to the same procedure as described above.[9] 2-Bromobutane (41.6 g, 0.3 mol), *tert*-

butanethiol (27 g, 0.3 mol) and NaOH (12.1 g, 0.3 mol) were used. The product was isolated in 70% (37 g) yield: bp 197-198 °C; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.98 (t, 3H, J = 7 Hz), 1.26 (d, 3H, J = 7 Hz), 1.31 (s, 9H), 1.52 (m, 1H), 1.68 (m, 1H), 2.74 (m, 1H); IR (vapor phase) ν 2971, 1461, 1369, 1287, 1165, 1006, and 790cm^{-1}. Anal. Calcd for $C_8H_{18}S_2$: C, 53.88; H, 10.17; S, 35.96. Found: C, 53.33; H, 10.23; S, 35.75.

***sec*-Butyl hexyl disulfide** was prepared using the standard procedure described for the preparation of butyl *tert*-butyl disulfide.[9] 1-Bromohexane (8.2 g, 0.05 mol) and *sec*-butanethiol (4.5 g, 0.05 mol) were used in the reaction. The product was isolated in 69% (7.2 g, 0.035 mol) yield: bp 222-223 °C; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.89 (t, 3H, J = 7 Hz), 0.98 (t, 3H, J = 7.5 Hz), 1.20-1.80 (m, 13H), 2.60-2.85 (m, 3H). Anal. Calcd for $C_{10}H_{22}S_2$: C, 58.19; H, 10.74. Found: C, 58.37; H, 10.69.

***tert*-Butyl hexyl sulfide** was prepared by alkylating the sodium salt of *tert*-butanethiol (9 g, 0.1 mol) with 1-bromohexane (16.6 g, 0.1 mol) in boiling ethanol (25 mL, 1 hr).[15] The product was isolated by pouring the reaction mixture onto 100 g of ice, and the crude oily layer was extracted with diethyl ether, dried, and filtered. Distillation of this material gaves 7.3 g (0.035 mol) of the pure sulfide in a 35% yield: bp 198-199 °C; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.26 (m, 15H), 1.55 (m, 2H), 2.50 (t, 2H, J = 7.5 Hz). Anal. Calcd for $C_{10}H_{22}S$: C, 68.89; H, 12.71. Found: C, 68.92; H, 12.63.

***tert*-Butyl 2-octyl sulfide** was prepared using the same procedure used for the synthesis of *tert*-butyl hexyl sulfide.[15] 2-Bromooctane (9.6 g, 0.05 mol) and *tert*-butanethiol (4.5 g, 0.05 mol) were used in the reaction. The product was isolated in 62% yield (6.3 g, 0.03 mol): ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.20-1.55 (m, 22H, max. 1.32, 9H), 2.65 (m, 1H). Anal. Calcd for $C_{12}H_{26}S$: C, 71.21; H, 12.95. Found: C, 71.61; H, 12.52.

***sec*-Butyl hexyl sulfide** was prepared using the standard procedure.[15] 1-Bromohexane (8.25 g, 0.05 mol) and *sec*-butanethiol (4.5 g, 0.05 mol) were used in the reaction. The product was isolated in a 81% yield (7.2 g, 0.04 mol): ^1H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 0.98 (t, 3H, J = 7.5 Hz), 1.26 (d, 3H, J = 6.5 Hz), 1.26-1.45 (m, 8H), 1.45-1.65 (m, 2H), 2.50 (t, 2H, J =7.5 Hz), 2.65 (m, 1H). Anal. Calcd for $C_{10}H_{22}S$: C, 68.89; H, 12.71. Found: C, 68.94; H, 13.20.

Hexyl cyclohexyl sulfide was prepared according to the standard procedure.[15] 1-Bromohexane (8.25 g, 0.05 mol) and cyclohexanethiol (5.8 g, 0.05 mol) yielded 8.2 g (0.04 mol) of pure sulfide: ^1H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.26-1.55 (m, 14H), 1.72 (m, 2H), 1.92 (m, 2H), 2.50 (t, 2H, J = 7.5 Hz), 2.60 (m, 1H); EI^+ (m/z): 209.8 (M^+). Anal. Calcd for $C_{12}H_{24}S$: C, 71.92; H, 12.07. Found: C, 71.68; H, 12.46.

***c*-Hexyl phenyl sulfide** was prepared according to the standard procedure.[15] The pure compound was obtained from the stock of this laboratory: bp 242-243 °C; ^1H NMR (300 MHz, $DCCl_3$) δ 1.30-1.50 (m, 5H), 1.62-1.70 (m, 1H), 1.79-1.88 (m, 2H), 2.01-2.11 (m, 2H), 3.12-3.22 (m, 1H), 7.20-7.35 (m, 3H), 7.42-7.50 (m, 2H); ^{13}C NMR (300 MHz, $DCCl_3$) δ 25.72, 25.95, 33.27, 126.44, 128.63, 161.76, 135.17. Anal. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39; S, 16.67. Found: C, 75.24; H, 8.64; S, 16.43.

2. General procedure for the reaction of disulfides or sulfides with atomic hydrogen and the quantitative GC analysis of the products - An aliquot of a solution of the disulfide or sulfide in acetone was placed in the U-shaped reactor. The reactor was cooled to −78 °C. The reaction system pressure was controlled at 3.00 torr by valve 1 (see Fig. II-4). The output of the microwave generator was adjusted to 80%. The reaction was carried out for 1 minute for disulfide reactions. After the reaction, the product mixture was transfered into a vial which was cooled in dry-ice and analyzed immediately by GC.

The product mixtures were analyzed using a 105 m × 0.25 mm × 0.5 μ m R_{tx}-1 capillary column. GC analysis was carried out using a Varian 6000 chromatograph equipped with a hydrogen flame detector interfaced to a Varian Vista CDS 401 chromatography data system. The area ratios were converted to mole ratios for quantitative determination by using correction factors which were obtained by preparing a standard solution of known concentrations of the authentic compounds and an internal standard.

The Reaction of Deuterium with Cyclohexyl phenyl sulfide - An aliquot solution of sulfide (0.1 M in acetone) was used for the reaction. The general procedure for the atomic hydrogen reaction was followed. Reaction time was 5 minute. The products were analyzed by GC and GC/MS.

3. Identification of Products - Hexane, octane, cyclohexane, benzene, 2-methylpropane, 1-butanethiol, *tert*-butanethiol, *sec*-butanethiol, 1-hexanethiol, cylohexanethiol, thiophenol, 2-octanethiol, di-*tert*-butyl disulfide, di-*sec*-butyl disulfide, diphenyl disulfide and di-1-butyl sulfide were identified by comparison of their GC retention time and their GC/MS and GC/IR with those of authentic compounds.

Dicyclohexyl disulfide was synthesized according to the literature procedure.[9] Cyclohexyl bromide (16.3 g, 0.1 mol) and cyclohexanethiol (11.62 g, 0.1 mol) were used in the reaction. The product was isolated in a 85% yield (20 g, 0.085 mol): bp195 °C/20 mm Hg; ^{1}H NMR (200 MHz, $DCCl_3$) δ 1.20-1.40 (m, 3H), 1.40-1.60 (m, 1H), 1.6-1.8 (m, 4H), 2.1-2.2 (m, 2H), 4.1-4.2 (m, 1H); EI+ (GC/MS, VG-70) m/z: 230 (M+), 148, 113, 83, 73, 67, 55 and 41; IR (vapor phase) ν 2940, 2871, 1453, 1341, 1263, 1198, and 993 cm^{-1}. Anal. Calcd for $C_{12}H_{22}S_2$: C, 62.55; H, 9.62. Found: C, 62.60; H, 9.46.

Dihexyl disulfide was synthesized according to the standard procedure.[9] 1-Bromohexane (16.5 g, 0.1 mol) and 1-hexanethiol (11.8 g, 0.1 mol) were used in the reaction. The product was isolated in a 80% yield (19 g, 0.08 mol): bp 228 °C/701 mm Hg; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.20-1.45 (m, 6H), 1.60-1.75 (m, 2H), 2.60-2.70 (t, 2H, J = 7.5 Hz); EI+ (GC/MS, VG-70) m/z: 234.1 (M+), 149.9, 117.0, 85.1, 55.0 and 43.0; IR (vapor phase) ν 2935, 2860, 1461, 1348, 1288, and 731 cm^{-1}. Anal. Calcd for $C_{12}H_{26}S_2$: C, 61.47; H, 11.18. Found: C, 61.19; H, 11.03.

***tert*-Butyl hexyl disulfide** was prepared according to the standard procedure.[9] 1-Bromohexane (16.5 g, 0.1 mol) and *tert*-butanethiol (9 g, 0.1 mol) were used in the reaction. The product was isolated in a 80% yield (16 g, 0.08 mol): bp 152 °C/20 mm Hg; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.20-1.45 (m, 15H), 1.55-1.65 (m, 2H), 2.60-2.70 (t, 2H, J = 7.5 Hz); EI+ (GC/MS, VG-70) m/z: 206 (M+), 150, 117, 85, 79 and 57; IR (vapor phase) ν 2935, 2872, 1463, 1367, 1288, 1167 cm^{-1}. Anal. Calcd for $C_{10}H_{22}S_2$: C, 58.19; H, 10.74. Found: C, 58.15; H, 10.65.

***tert*-Butyl 2-octyl disulfide** was prepared from *tert*-butanethiol and 2-octanethiol according to the literature procedure.[13,14] 2-Octanethiol was prepared according the literature procedure.[13] A mixture of 2-bromooctane (77.2 g, 0.4 mol) and a solution of thiourea (10.1 g, 0.5 mol) in 25 mL of water was heated to reflux with vigorous stirring for 2 hours. A solution of 30 g of sodium hydroxide in 30 mL of water was added, and the reaction mixture was heated to reflux with stirring for a further 2 hours. After cooling, the upper layer of crude 2-octanethiol was separated and dried. 2-Octanethiol was isolated in a 70% yield (40 g, 0.28 mol). A mixture of 2-octanethiol (10 g, 0.07 mol) and *tert*-butanethiol (6.3 g, 0.07 mol) was added to 10 mL of H_2O_2 (30%) solution at 50-60 °C in 2 hours, and the reaction mixture was again heated with stirring for a further 2 hours. The crude disulfide which separated as an oil was washed, dried and filtered. Distillation of this crude material gaves 4.7 g (0.02 mol) of pure disulfide in a 30% yield:[15] bp 177 °C/90 mm Hg; ^1H NMR (200 MHz, $DCCl_3$): δ 0.90 (t, 6H, J = 7 Hz), 1.20-1.70 (m, 22H), 2.70-2.80 (m, 1H); EI^+ (GC/MS, VG-70) m/z: 234.2 (M^+), 178.2, 146.1, 113.1, 71.1, 57.0 and 41.0; IR (vapor phase) ν 2934, 2871, 1460, 1368, 1165, and 1017 cm^{-1}.

Di-2-octyl disulfide was prepared by the H_2O_2 oxidation of 2-octanethiol (10 g, 0.07 mol).[14] The product was isolated in a 50% yield (10 g, 0.035 mol): bp 198-200 °C/90 mm Hg; ^1H NMR (200 MHz, $DCCl_3$): δ 0.90 (t, 6H, J = 7 Hz), 1.20-1.70 (m, 26H), 2.70-2.82 (m, 2H); EI^+ (GC/MS, VG-70) m/z: 290 (M^+), 178, 113, 71, 57 and 41; IR (vapor phase) ν 2934, 2868, 1460, 1378, 1271, and 1015 cm^{-1}. Anal. Calcd for $C_{16}H_{34}S_2$: C, 66.13; H, 11.74. Found: C, 66.24; H, 11.83.

Hexyl cyclohexyl disulfide was prepared according to the standard procedure.[9] 1-Bromohexane (16.5 g, 0.1 mol) and cyclohexanethiol (11.6 g, 0.1 mol) were used in the reaction. The product was isolated in a 75% yield (17 g, 0.075 mol): bp 205-207 °C at 701 mm Hg. ^1H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.20-1.40 (m, 12H), 1.55-1.85 (m, 4H), 1.90-2.10 (m, 2H), 2.50-2.60 (m, 1H), 2.70 (t, 2H, J = 7.5 Hz); EI^+ (GC/MS, VG-70) m/z: 232.0 (M^+), 150.1, 117.1, 83.1, 55.0; IR (vapor phase) ν 2939, 2865, 1453, 1343, 1264, 1199, 994, and 887 cm^{-1}. Anal. Calcd for $C_{12}H_{24}S_2$: C, 62.01; H, 10.41. Found: C, 61.70; H, 10.80.

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APPENDIX II-1

A. The calculation of the concentration of atomic hydrogen in the reaction:

When neat 1-octene (7.10 g, 0.063 mol) was allowed to react with atomic hydrogen, 1.1% conversion was obtained after 4 minute reaction time (see Table II-1, reaction 1).The concentration of the starting material is:

$$[\text{1-octene}]_o = (0.71 \text{ g/mL} / 112 \text{ g/mol}) \times 10^3 = 6.38 \text{ M}$$

The velocity of the reaction: $\Delta[P]/\Delta t = \{[\text{1-octene}]_o - [\text{1-octene}]_1\}/\Delta t = \{1.1\ \% \times [\text{1-octene}]_o\}/240 = 2.9 \times 10^{-4} \text{ M s}^{-1}$

The disproportionation and combination products are 80% of the total products (see Table II-1, reaction 1). Therefore, the velocity of disproportionation and combination equals 2.1×10^{-4} M s^{-1}. Alkyl-alkyl radical disproportionation and combination rates are diffusion controlled reactions. Diffusion in 1-octene at −78 °C is calculated as follows:[1]

The viscosity of 1-octene $\eta = \exp[A + B/T + C \ln T + DT^E]$ Pa s^{-1} Where A = 1.5841E+01, B = −1.9440E+02, C = −4.0180E+00, D = 1.9000E −27, and E = 1.0000E+01. At −78 °C, the viscosity of 1-octene $\eta = 1.769 \times 10^{-3}$ Pa s^{-1}. The rate constant for a diffusion-controlled reaction is given by:[2]

$$k_{diff} = 8RT \times 10^3/(3\eta) \text{ M}^{-1}\text{s}^{-1} = 2.44 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$$

Where R = 8.314 J K^{-1} mol^{-1}. Applying spin correction, then $k_{R\cdot} = k_{diff}/4 = 6.1 \times 10^8$ M^{-1} s^{-1} at −78 °C. The concentration of alkyl radicals is:

$$[R\cdot] = (2.1 \times 10^{-4} / 6.1 \times 10^8)^{1/2} = 5.9 \times 10^{-7} \text{ M}$$

The products from the reaction of atomic hydrogen with an alkyl radical are 20% of the total products, see Table II-1, reaction 1. Therefore, the velocity of the reaction of atomic hydrogen with an alkyl radical equals 5.8×10^{-5} M s^{-1}. Then the concentration of atomic hydrogen is:

$$[H\cdot] = 5.8 \times 10^{-5} / [10^{9} \times 5.9 \times 10^{-7}] = 1.0 \times 10^{-7}\ M$$

The same calculations done for reactions 2-4 in Table II-1 gave concentration of $[H\cdot] = 1.0 - 1.5 \times 10^{-7}$ M.

The rate of combination of radical with atomic hydrogen can be estimated as follows:

$$\text{Rate} = k\ [H\cdot]\ [R\cdot] = 10^{10} \times 10^{-7} \times 10^{-7} = 10^{-4}\ M\ s^{-1}$$

The rate constant for the reaction of methyl radical with molecular hydrogen was reported,[3] $k = 3.3 \times 10^{9} \exp(-12{,}200/RT)$ M^{-1} s^{-1}. The calculated rate constant at −78 °C is 7.0×10^{-5} M^{-1} s^{-1}. The rate of reaction of radical with molecular hydrogen can be estimated as follows:

$$\text{Rate} = k\ [H_2]\ [R\cdot] = 7.0 \times 10^{-5} \times 0.04 \times 10^{-7} = 2.8 \times 10^{-13}\ M\ s^{-1}$$

Where the maximum concentration of molecular hydrogen is less than 0.04 M, the saturation concentration at −78 °C.[4] Therefore the reaction of molecular hydrogen with alkyl radical is unimportant.

B. The calculation of the velocity of alkane formation from the reaction of atomic hydrogen with unsymmetric sulfide:

The rate of formation of alkane can be calculated when [H•] and [R•] are known.

$$\begin{aligned} d[RH]/dt &= k_{RH} [H\bullet] [R\bullet] \\ &= 10^9 \times (1 \times 10^{-7}) \times (5.6 \times 10^{-7}) \\ &= 5.6 \times 10^{-5} \text{ M s}^{-1} \end{aligned}$$

Formation of alkane from transfer with thiol is a much more favorable process.

$$\begin{aligned} d[RH]/dt &= k_{RSH} [RSH] [R\bullet] \\ &= 10^6 \times (10^{-2}) \times (5.6 \times 10^{-7}) \\ &= 5.6 \times 10^{-3} \text{ M s}^{-1} \end{aligned}$$

Where $k_{RSH} = 10^6$ M^{-1} s^{-1}, and [RSH] = 10^{-2} M was the concentration of thiols at half conversion.

APPENDIX III-1

The calculation of the transfer rate for poly(methyl methacrylate) radicals:

The chain transfer constants for CCl_4, $C^o = k_t/k_p = 4700, 1500$ at 20 °C and 0 °C, were reported for poly(methyl methacrylyl) radicals.[3] From equation (1):

$$\ln [C^o_1/C^o_2] = - \Delta Ea\ (1/T_1 - 1/T_2)/R \qquad (1)$$

$\Delta Ea = Ea(t) - Ea(p) = 9.08$ kcal mol^{-1} and $C^o_{(-78)} = 1.86$ was calculated. The Arrhenius equation for propagation reactions, $k_p = 2.0 \times 10^6 \exp(-4700/RT)$ M^{-1}s^{-1}, was reported.[5] The propagation rate constant at –78 °C, $k_{p(-78)} = 10.79$ M^{-1}s^{-1}, was obtained. Therefore, the transfer rate constant at –78 °C, $k_{t(-78)} = k_{p(-78)} \times C^o_{(-78)} = 10.79 \times 1.86 = 20.07$ M^{-1}s^{-1}, was calculated.

APPENDIX III-2

The calculation of the transfer rate for polystyrenyl radicals:

The chain propagation constants for CCl_4, k_p = 13, 44 at 0 ^oC and 25 ^oC, were reported for polystyrenyl radicals.[4] From equation (1):

$$\ln [k_{p1}/k_{p2}] = - Ea(p)\ (1/T_1 - 1/T_2)/R \qquad (1)$$

$Ea(p) = 7.88$ kcal mol^{-1} and $k_{p(-78)} = 3.9 \times 10^2\ M^{-1}s^{-1}$ was calculated. The chain transfer constant at 60 ^oC, $C^o{}_{60} = k_t/k_p = 90$ and $\Delta Ea = Ea(t) - Ea(p) = 5.0$ kcal mol^{-1}, was reported.[6] The chain transfer constant at –78 ^oC, $C^o{}_{(-78)} = 0.43$, was obtained. Therefore, the transfer rate constant at –78 ^oC, $k_{t(-78)} = k_{p(-78)} \times C^o{}_{-78} = 3.9 \times 10^2 \times 0.43 = 0.017\ M^{-1}s^{-1}$, was calculated.

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