

Formation of Three-Membered Rings by S_{HI} Displacement. Reverse of Cyclopropyl Ring Opening¹

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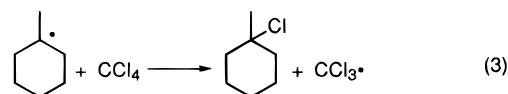
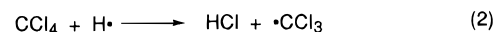
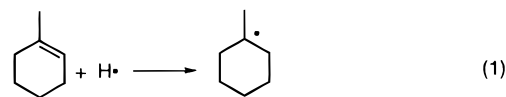
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The general methods, photoinitiated or peroxide-initiated free radical chain additions of halomethanes to olefins, yield 1,2-addition products at temperatures ranging from 20 to 100 °C. At lower temperatures, –42 to –104 °C, a competitive reaction, subsequent to the addition of CCl₂X[•], yields alkylcyclopropanes. The reactions of 1-octene or 1-hexene and 1-methylcyclohexene with atomic hydrogen carried out in the presence of several transfer agents (CCl₄, CCl₃Br, CCl₂Br₂) initiate a radical chain addition of CCl₂X[•] and yield cyclized materials resulting from the S_{HI} displacement of halogen by a carbon-centered radical. The radical displacement of a halogen on carbon, the reverse of homolytic displacement on cyclopropyl carbon, is dominant at low temperatures. The rate constants for cyclization (*k_c*) vs transfer with halomethane (*k_t*) showed isokinetic temperatures of –46 °C (CCl₄, 1-hexene); –35 °C (CCl₄, 1-methylcyclohexene). The isokinetic temperatures for the reactions of the two substrates carried out in the presence of BrCCl₃ were calculated as –204 °C (1-octene) and –109 °C (1-methylcyclohexene).

The mechanisms for the regioselective additions of atomic hydrogen to 1-octene² and 1-methylcyclohexene^{1,3} were recently reported. Hydrogen atoms generated in a flow system using a microwave plasma and passed in a stream over a stirred solution of the substrate, either neat or in solvent acetone, yield a mixture of reduction products. The additions were found to be highly regioselective (*i.e.*, H[•] added exclusively to the least highly substituted end of the double bond).^{2,3}

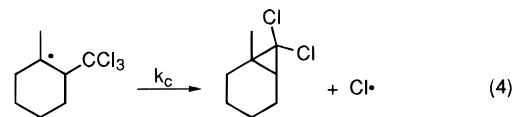
Reactions in the Presence of CCl₄ and CCl₃Br. In preliminary experiments, in order to substantiate whether atomic hydrogen added exclusively to the 2-position of 1-methylcyclohexene (eq 1), the reactions were carried out in acetone containing varying concentrations of a transfer agent, carbon tetrachloride. Although atomic hydrogen reacts with carbon tetrachloride (eq 2) to yield HCl, C₂Cl₆, and CCl₃H, its reaction with olefins is much faster, since only small amounts of HCl could be detected. Alkyl radical abstraction of a chlorine atom to form the trichloromethyl radical (eq 3) accounts for 82–100% of the products formed from the reactions involving carbon tetrachloride. The product distribution of the reactions is shown in Table 1. The HCl that was detected by titration, however, did not react with the olefin since control experiments showed that no reaction occurred between 1-methylcyclohexene and HCl under the experimental conditions (neat olefin, –78 °C, 30 min). Since the only monochlorinated product was 1-chloro-1-methylcyclohexane (*i.e.*, no 2-chloro-1-methylcyclohexane could be detected), the addition of H[•] appeared to take place at the secondary carbon of the double bond (*e.g.*, eqs 1 and 3). In addition to the expected products (chloroform, methylcyclohexane, methylenecyclohexane, 1-chloro-1-

methylcyclohexane, hexachloroethane, and the 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 1.



Since atomic hydrogen reacts by addition to the least hindered olefinic position, eq 1, and the tertiary alkyl radical reacts with carbon tetrachloride, eq 3, both products of the tertiary alkyl radical and the CCl₃[•] radical are predictably formed. The CCl₃[•] radical is also formed, but more slowly, by the reaction of atomic hydrogen with CCl₄, eq 2.

The unexpected product, 7,7-dichloro-1-methylbicyclo[4.1.0]heptane appears to be the result of a radical displacement on carbon (eq 4). Although examples of this



reaction type are rare, they are not unprecedented. Johnson *et al.*^{4,5} reported that two isomeric 1-cyano-2,2-dimethyl-3-(2',2',2'-trichloroethyl)cyclopropanes were formed through a radical cyclization pathway from the reactions of 2-bromo-3,3-dimethyl-4-pentenitrile with

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(1) Taken in part from the Ph.D. Dissertation of L. Zhang, University of Alberta, 1994.








(2) Tanner, D. D.; Zhang, L. *J. Am. Chem. Soc.* **1994**, *116*, 6683.

(3) Tanner, D. D.; Zhang, L.; Kandanarachchi, P. *J. Phys. Chem.* **1996**, *100*, 11319.

(4) Bury, A.; Corker, S. T.; Johnson, M. D. *J. Chem. Soc., Perkin Trans. 1* **1982**, 645.







(5) Bury, A.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1980**, 498.

Table 1. Product Distribution from the Reaction of Atomic Hydrogen with 1-Methylcyclohexene (−78 °C) in the Presence of Carbon Tetrachloride^a

[CCl ₄] (M)	CCl ₄ Conversion (mol × 10 ⁴)	Products ^b (mol × 10 ⁴)								
		HCCl ₃ A				C ₂ Cl ₆ C				
0.06	1.30	0.32	1.94	0.51	1.02	0.33	0.21	0.05	0.15	0.82
0.13	2.00	0.53	1.77	0.45	1.69	0.51	0.24	0.11	0.06	0.89
0.31	9.07	2.60	3.92	0.72	8.85	2.08	1.17	0.57	0.13	1.04
0.50	8.70	1.34	1.70	0.34	6.07	1.71	0.65	0.30	0.03	1.06

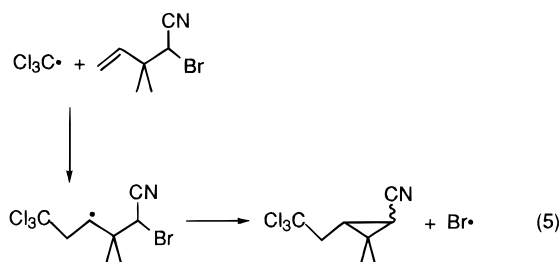
^a The concentration of 1-methylcyclohexene is 1.00 M in acetone. ^b Trace of HCl was detected. ^c Products arising from the disproportionation of the 1-methyl-6-(trichloromethyl)cyclohexyl radical were detected in ~1:0.4:0.9 ratio (1-methyl-2-trichlorocyclohexene, 1-methylene-2-(trichloromethyl)cyclohexane, 1-methyl-6-(trichloromethyl)cyclohexene).

Table 2. Product Distribution from the Reactions of H[•] with 1-Methylcyclohexene in the Presence of CCl₄ (4 M)^a

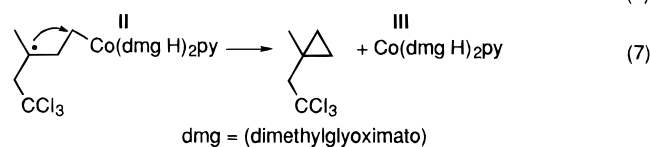
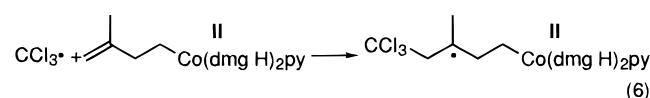
Temp (°C)	Products (mol × 10 ⁵)								
	HCCl ₃				C ₂ Cl ₆				D/E
-78	68.6	923	12.7	757	387	44.1	0.713	3.94	61.8
-78	7.88	11.65	2.43	83.7	45.5	5.09	0.08	.09	64.3
-62	7.22	39	23	61.4	17	3.05	.38	tr	8.0
-48	3.03	20	19	12.4	4.9	0.79	0.95	tr	0.83

^a Concentration of 1-methylcyclohexene is 1.060 M in acetone.

carbon tetrachloride, bromotrichloromethane, or trichloromethanesulfonyl chloride, eq 5. A similar cyclization

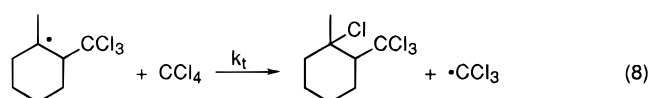
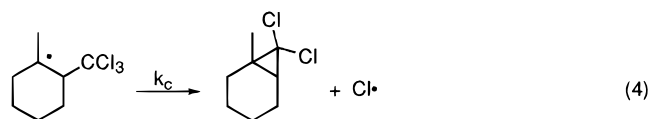


was also reported⁶ which involved an S_{HI} displacement of cobaloxime by a carbon-centered radical, eqs 6 and 7.



The observation that at −78 °C ring closure, k_c , takes place (eq 4) in preference to 1,2-addition, k_t , (eq 8), is not

surprising since the rate of transfer of the sterically hindered tertiary radical is expected to be much slower than that of an intramolecular displacement–cyclization.^{4–7}



In order to increase the possibility that the transfer rate k_t [CCl₄], will compete with the rate of cyclization, the concentration of [CCl₄] was increased to 4 M, see Table 2. Under these conditions both the cyclized product and the 1,2-addition product are formed. An even higher ratio of 1,2-addition/cyclization product is obtained when bromotrichloromethane, a more favorable halogen donor, is used as a transfer agent, see Table 3.

The cyclization mechanism was further substantiated by carrying out the hydrogenation of 1-hexene in the

(7) (a) The transfer rate constant for a primary radical^{7b} with CCl₄ at −78 °C is 8×10^1 and would be even slower with a tertiary radical. A transfer rate, k_t [CCl₄], at these concentrations would not be expected to propagate a chain. (b) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

(6) Johnson, M. D. *Acc. Chem. Res.* **1983**, *16*, 343.

Table 3. Reaction of 1-Methylcyclohexene (1.06 M) with H[•] in Solvent Acetone with Added BrCCl₃ (1.06 M)





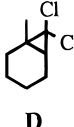








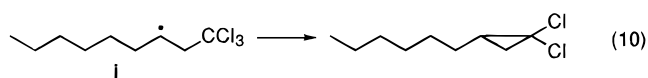
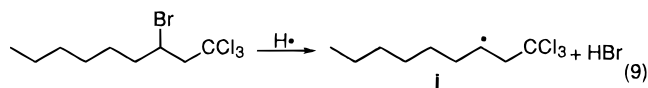
Temp (°C)	Time (min.)	Products (mol × 10 ⁴)									F/D
		CHCl ₃					C ₂ Cl ₆				
-42	10	8.14	6.22	4.80	0.64	0.07	1.44	1.54	16.44	trace	10.65
		20.31	3.86	9.51	6.06	0.75	4.04	1.90	17.11	trace	9.02
-78	30	15.47	14.91	9.17	19.60	1.52	20.60	2.55	8.73	trace	3.42
		19.95	22.07	10.39	49.25	3.91	51.90	3.23	11.90	0.08	3.69
-104	30	8.31	6.14	12.30	16.19	0.23	8.83	0.74	1.01	0.08	1.37
		4.68	10.95	12.89	24.66	0.54	19.30	1.40	2.00	0.05	1.43

Table 4. Product Distribution from the Reactions of Atomic Hydrogen with 1-Hexene in the Presence of Carbon Tetrachloride (2 M).

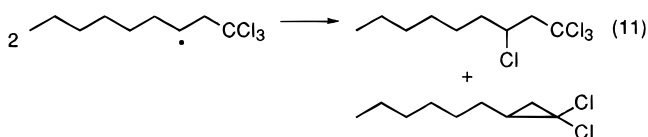
Temp (°C)	Time (hr)	Products (mol × 10 ³)									A/B	
		HCCl ₃					C ₂ Cl ₆			Others		
-78	1	1.40	48.1	7.20	0.97	0.054	0.036	1.50	0.27	0.0151	0.43	3.60
		1.42	44.4	8.30	0.81	0.051	0.033	1.20	0.21	0.0147	1.17	3.50
		2.04	90.3	16.70	2.54	0.18	0.24	4.10	0.78	0.044	2.92	4.10
-95	1	1.97	54.5	9.00	1.80	0.17	0.06	4.00	0.63	0.009	2.67	19.0
		1.95	43.0	8.00	1.00	0.15	0.019	2.9	0.15	0.0067	3.65	21.8
		3	14.6	188.8	33.5	6.50	0.54	0.80	22.7	2.37	0.027	2.13
-104	3	5.99	146.7	55.5	3.1	0.42	0.47	38.1	1.86	0.0099	0.04	42.3
		1.41	150.7	30.4	3.4	0.45	1.50	40.5	2.29	0.0110	0.51	39.3

presence of CCl₄ or of 1-octene in the presence of BrCCl₃. The addition of a trichloromethyl radical to the terminal position of a monosubstituted olefin yields a secondary alkyl radical. Since the secondary alkyl radical is more reactive and less sterically crowded than the tertiary radical formed from the addition of CCl₃[•] to 1-methylcyclohexene, it is predictable that a higher ratio of 1,2-addition, *P*₁₂, of CCl₃X to cyclization, *P*_c, can be achieved. The ratios of *P*₁₂/*P*_c obtained from the analysis of the reaction mixture from 1-octene and 1-hexene are listed in Table 4 and 5.

To test the hypothesis that the three-membered-ring system was formed *via* a radical displacement, 3-bromo-1,1,1-trichlorononane was synthesized and allowed to react with atomic hydrogen. Since it had previously been demonstrated that a secondary alkyl bromide readily reacts with atomic hydrogen,² it was assumed that radical displacement of bromine would likely form the secondary radical, **i**. As predicted, 1,1-dichloro-2-hexylcyclopropane resulting from the reaction of radical **i** was formed, although not as the exclusive product, eqs 9 and 10. Since a majority of the products formed from **i** are



disproportionation products, another pathway for the formation of the cyclopropane can be envisioned. Disproportionation between two molecules of **i** could also lead to a cyclized product, eq 11. This pathway, although

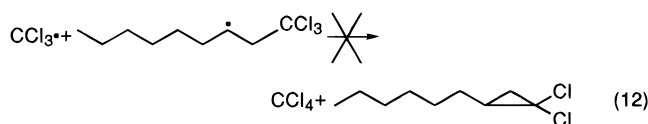


plausible, can be ruled out since no tetrachlorinated product could be detected. This conclusion, that the cyclized material was not a product of disproportionation, was further substantiated since in reactions carried out with CCl₃Br no CCl₄ could be detected (see eq 12).

Table 5. Product Distribution of the Reaction of Atomic Hydrogen with 1-Octene in Presence of Bromotrichloromethane

Temp (°C)	[BrCCl ₃] M	Products (mol × 10 ⁵) ^c												
		HCCL ₃	RC ₂ H ₅			C ₂ Cl ₆								
-42	0.50 ^a	tr	22.4	2.28	0.59	5.74	8.26	0.65	0.60	0.67	0.20	32.7	54.5	1.92 × 10 ³
-78	0.25 ^b	0.67	11.3	2.06	1.34	17.7	31.5	0.83	0.46	1.55	0.18	8.75	19.0	2.63 × 10 ²
-94	0.50 ^b	2.93	21.8	5.26	2.24	75.5	125	0.28	1.63	1.74	0.28	50.3	30.8	6.00 × 10 ¹

^a BrCCl₃ in neat 1-octene. ^b BrCCl₃ in 3 M solution of 1-octene in acetone. ^c R = C₆H₁₃, R' = C₅H₁₁.



The homolytic 1,2-addition to olefins of both CCl₄ and CCl₃Br are standard synthetic reactions.^{8,9} No geminal dichlorocyclopropanes have been reported as products from these additions. The standard conditions used in these synthetic reactions prescribe reaction between a 2:1 mixture of CCl₃X:olefin (CCl₄, 90–100 °C, benzoyl peroxide) or (CCl₃Br, 60–70 °C, acetyl peroxide or *hv*).

At –78 °C the cyclization reaction for CCl₄ is favored over 1,2-addition, see Tables 4 and 5. Since it appears that the temperature at which the two competing reactions (addition and cyclization) are carried out could be the major factor determining the ratio of these two products, the temperature dependence of their formation was determined. At –78 °C the cyclization reaction for CCl₄ is favored over 1,2-addition; this temperature appears to be lower than the isokinetic temperature at which the two rates become equal or reversed. When the reaction was carried out at several temperatures, a plot of the activation energy differences for addition vs cyclization could be calculated. As suspected, the ratio of rate constants is reversed at the isokinetic temperature: –46 °C (CCl₄, 1-hexene); –35 °C (CCl₄, 1-methylcyclohexene), see Figure 1, part a.

The isokinetic temperature for the hydrogen atom promoted reaction of BrCCl₃ can likewise be determined for the two substrates: –204 °C (BrCCl₃, 1-octene); –109 °C (BrCCl₃, 1-methylcyclohexene), see Figure 1, part b. The cyclization rate constants for both substrates, k_c, can be calculated if the rate constants for transfer, k_t, are known (eq 13). The transfer rate constants, k_t, could be

$$k_c = k_t(XCCl_3) \frac{[P_c]}{[P_{12}]} \quad (13)$$

calculated since the temperature dependence of the chain transfer constants, C = k_t/k_p, has been reported for the two transfer agents with the secondary radical formed during the polymerization

$$\ln[C_{11}^{\circ}/C_{12}^{\circ}] = \Delta E_a(1/T_1 - 1/T_2)/R \quad (14)$$

(8) Walling, C.; Huyser, E. S. *Organic Reactions*, Vol. 13; Wiley: New York, 1963.

(9) Sosnovsky, G. *Free Radical Reactions in Preparative Organic Chemistry* Macmillan: New York, 1964.

of vinyl acetate (see eq 14),¹⁰ where ΔE_a = E_{a(t)} – E_{a(p)} = 9.08 kcal mol⁻¹ for CCl₄ and 1.1 kcal mol⁻¹ for BrCCl₃. Since the Arrhenius equation for the polymerization propagation reaction, k_p = 2.0 × 10⁶ exp(–4700/RT) M⁻¹ s⁻¹, has also been reported,¹¹ the temperature dependence of the transfer rate constant is determined, see Table 6. Also listed in Table 6 is a comparison of the experimental and calculated ratios of rate constants of cyclized/1,2-addition products.

Arrhenius plots of the rates of cyclization of the radicals resulting from the addition of •CCl₃ to 1-octene or 1-hexene and 1-methylcyclohexene (Figure 2) generated from either transfer agent (CCl₄ and CCl₃Br) can be constructed.

The activation parameters for cyclization, calculated from the experimental data (Table 6), for either the (2,2,2-trichloroethyl)heptyl or the (2,2,2-trichloroethyl)pentyl radical (E_c = 6.6 ± 0.76 kcal/mol; log A_c = 9.7 ± 0.9 eu) generated in the presence of CCl₄ or CCl₃Br are consistent with cyclization reactions where only 2° of rotational freedom are frozen in the transition state.¹² The rate constant for cyclization, using these activation parameters, was k_c(25 °C) = 9.4 × 10⁴ s⁻¹, regardless of which transfer agent was used. An analysis of the activation parameters calculated for the cyclization of the 1-methyl-2-(2',2',2'-trichloromethyl)cyclohexyl radical (E_c = 3.2 ± 0.8 kcal/mol; log A_c = 7.4 ± 0.1 eu), see Table 6 and Figure 2, was less straight forward since the transition state rigidity for the reaction of a substituted cyclohexyl radical could not be well defined.¹³ The rate constant obtained for the substituted cyclohexyl radical (k_c 25 °C) = 6.4 × 10⁴ s⁻¹) was also insensitive to the transfer agent used. A possible error in the determination of the cyclization rate constant could be introduced during the reaction of BrCCl₃ with the olefin, since subsequent to 1,2-addition further reaction (*i.e.* eqs 10 and 11) of the bromide with H• could lead to cyclization. This complication (at low conversion) can be ruled out since k_c is constant for reactions where either CCl₃Br or CCl₄ is used as the transfer agent (see Figure 2).

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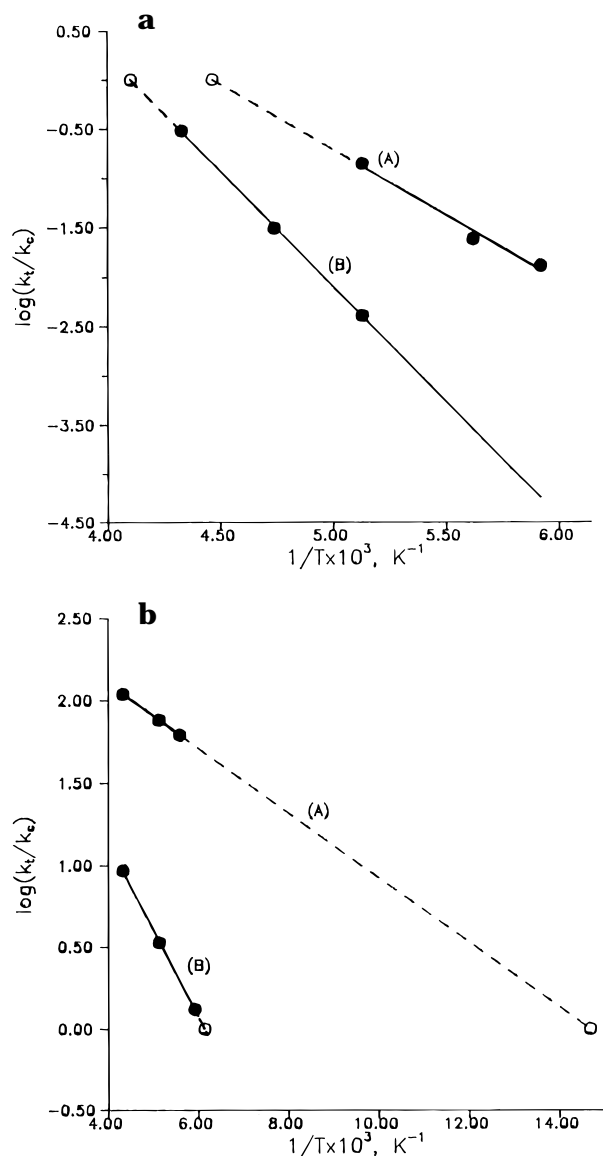


Figure 1. (a) Variation of $\log(k_t/k_c)$ with $1/T$ for the reaction of 1-hexene (A) and 1-methylcyclohexene (B) with hydrogen atoms in the presence of carbon tetrachloride. The dotted line represents the extrapolation to the isokinetic temperature. (b) Variation of $\log(k_t/k_c)$ with $1/T$ for the reaction of 1-octene (A) and 1-methylcyclohexene (B) with hydrogen atoms in the presence of bromotrichloromethane. The open circles represent extrapolated values to the isokinetic temperatures.

Reaction in the Presence of CCl_2Br_2 . In order to generalize the mechanism of the cyclization pathway, the hydrogenations were carried out in the presence of CCl_2Br_2 . As expected, both 1,2-addition and cyclization occurred at low concentrations of transfer agent, CCl_2Br_2 , see Table 7.

Reaction in the Presence of CBr_2F_2 . More recently Wu *et al.*¹⁴ reported that at 0 °C the Zn-promoted reaction of dibromodifluoromethane with several olefins gave not only 1,2-addition but small amounts of difluorocyclopropanated addition. The authors proposed a dual mechanism, a radical reaction to give 1,2-addition (eqs 15 and 16) and disproportionation (eq 17) or Zn-promoted reduction (eq 18 or 19) to give cyclopropanation. Since carbene addition (eq 20) did not give the same product stereo-

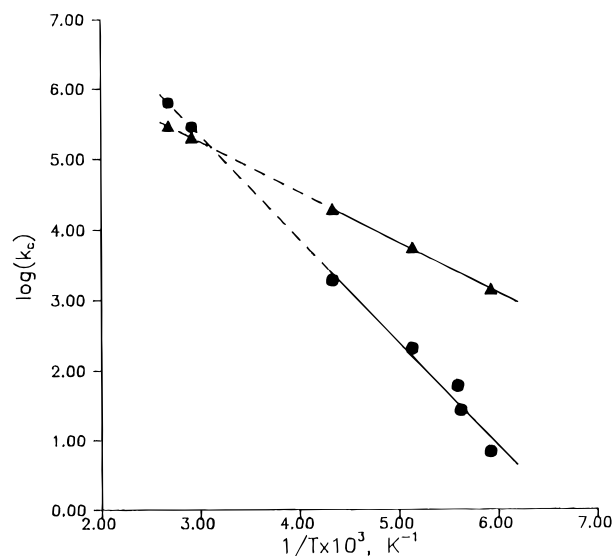
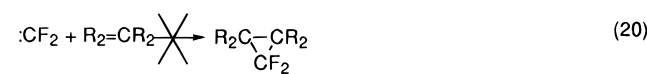
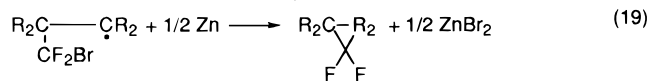
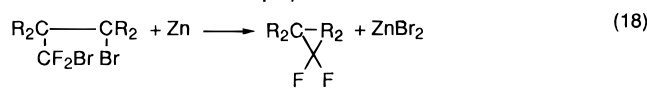
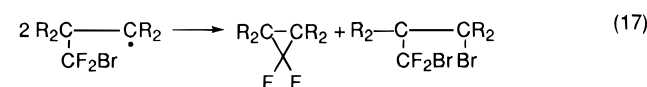
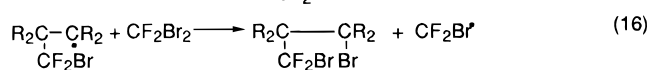
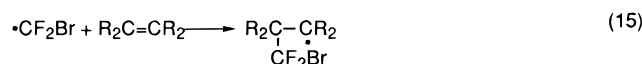


Figure 2. Arrhenius plot for the cyclization of 1-methyl-2-(trichloromethyl)cyclohexyl radical (▲), and (2,2,2-trichloroethyl)heptyl radical and (2,2,2-trichloroethyl)pentyl radical, (●). The dotted line represents the extrapolation of the rate constant, k_c , to 70 and 100 °C.

chemistry as the Zn-promoted reduction, this pathway was likewise ruled out, eq 20. The dual mechanism was



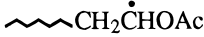
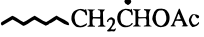
chosen and substantiated since when dibromodifluoromethane was allowed to react with an olefin under the usual radical conditions (3% benzoyl peroxide, 80 °C, 72 h) only 1,2-addition products were obtained;¹⁴ no cyclopropanation products were detected. These results did not appear to be a significant test for the mechanism, since radical addition of halomethanes under these conditions do not yield cyclized materials. When difluorodibromomethane was allowed to react with H[•] and 1-octene (-78 °C), only 1,2-addition could be detected. In agreement with Wu, *et al.* the cyclopropanation in their reaction was no doubt due to the presence of Zn (eq 18 or 19).

Experimental Section

Materials. 1-Methylcyclohexene (Fluka, +99%), carbon tetrachloride (Aldrich, HPLC grade, +99%), 1-octene (Phillips, research grade, +99%), 1-hexene (Aldrich, +99%), bromotrichloromethane, (Aldrich, spectrophotometric grade, +99.5%),











(14) Wu, S. H.; Liu, W. A.; Jiang, X. K. *J. Org. Chem.* **1994**, *59*, 854.

Table 6. Determination of the Transfer Rate Constants and Cyclization Rate Constants Using a Model Secondary Radical, Poly(vinyl acetate)

Model	Reactant	Donor	Temp. (°C)	E _a (kcal/mol)	k _t (M ⁻¹ s ⁻¹)	k _c ^a (s ⁻¹)	log k _t /k _c ^b
	1-hexene	CCl ₄	100	13.8	4.7 × 10 ⁸	(2.8 × 10 ⁶)	(2.2)
		(2 M)	-78		2.0 × 10 ¹	1.5 × 10 ²	-0.87
			-95		6.7 × 10 ⁻¹	2.7 × 10 ¹	-1.61
			-104		8.4 × 10 ⁻²	6.8	-1.91
	1-octene	CCl ₃ Br	70	5.82	1.3 × 10 ⁷	(9.5 × 10 ⁴)	(2.14)
		(0.8 M)	-42		2.1 × 10 ⁵	1.9 × 10 ³	2.04
			-78		2.0 × 10 ⁴	2.6 × 10 ²	1.89
			-94		3.7 × 10 ³	6.0 × 10 ¹	1.79
	1-methylcyclohexene	CCl ₄	100	13.8	4.7 × 10 ⁸	(4.7 × 10 ⁴)	(4.00)
		(4 M)	-42		5.1 × 10 ³	1.7 × 10 ⁴	-0.54
			-78		2.0 × 10 ¹	4.9 × 10 ³	-2.39
		BrCCl ₃	70	5.82	1.3 × 10 ⁷	(2.5 × 10 ⁵)	(1.71)
		(1.06 M)	-42		2.1 × 10 ⁵	2.1 × 10 ⁴	1.00
			-78		2.0 × 10 ⁴	6.0 × 10 ³	5.2 × 10 ⁻¹
		-104		1.8 × 10 ³	1.4 × 10 ³	1.1 × 10 ⁻¹	

^a Values in parentheses are extrapolated from Figure 1 and 2. ^b Calculated from the experimental values (Table 4 and 5), using eq 12.

Table 7. Product Distribution of the Reaction of Atomic Hydrogen with 1-Octene (-78 °C) in the Presence of Dibromodichloromethane^a.

[Br ₂ CCl ₂] M	Products (mol × 10 ⁵) ^b													k _t /k _c (M)
	HCClBrCl ₂	RC ₂ H ₅			C ₂ Br ₂ Cl ₄									
0.10	1.57	6.10	1.62	0.39	3.28	20.7	0.48	0.30	0.11	0.05	1.14	3.80	38.0	
0.30	0.87	6.95	1.99	0.55	5.23	15.5	-	0.48	0.74	0.07	4.60	9.58	31.9	
0.50	2.20	51.0	20.5	7.00	24.9	58.0	8.15	4.20	5.85	0.50	73.9	17.60	35.2	
1.00	2.98	4.95	4.88	0.65	34.8	15.6	0.49	0.11	0.45	0.19	4.24	38.5	38.5	
Ave. 35.9±2.4														

^a All solutions were in acetone and the hydrogen flow rate was kept at 4 mL/min. The reaction times varied from 3 to 15 min. ^b R = C₆H₁₃; R' = C₅H₁₁.

nonane (Phillips, research grade, +99%), and dodecane (Phillips research grade, +99%) were checked for purity (GC) prior to use.

Identification and Characterization of the Reaction Products. Chloroform, methylcyclohexane, methylenecyclohexane, hexachloroethane, 1-bromooctane, 2-bromooctane, *trans*- and *cis*-2-octene, *n*-octane, *n*-hexane, 1,1'-dimethylbicyclohexyl,³ *dl*- and *meso*-7,8-dimethyltetradecane, and² 7-methylpentadecane² were identified by a comparison of their retention times on GC, GC/MS, and GC/IR with either the following synthesized materials or with available authentic samples.

7,7-Dichloro-1-methylbicyclo[4.1.0]heptane was prepared according to the literature procedure reported for the

addition of dichlorocarbene to cyclohexene.¹⁵ The product was isolated in 62% yield: ¹H NMR (400 MHz, CDCl₃) δ 1.18–1.42 (m, 8H), 1.64–1.72 (m, 2H), 1.79–1.98 (m, 2H); ¹³C NMR (300 MHz, CDCl₃) δ 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 C₈H₁₂Cl₂: C, 53.65; H, 6.75. Found: C, 53.60; H, 6.94.

1-Chloro-1-methyl-2-(trichloromethyl)cyclohexane was prepared by the peroxide-initiated addition of CCl₄ to 1-methylcyclohexene (110 °C) according to the literature procedure reported for the reaction of 1-octene:^{16a} bp 95 °C/0.2 mmHg; EI⁺ (GC/MS, VG-70) *m/z* 250 (C₈H₁₂³⁵Cl₃³⁷Cl), 248 (C₈H₁₂³⁵-

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$\text{Cl}_3^{37}\text{Cl}$) 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} . Anal. Calcd for $\text{C}_8\text{H}_{12}\text{Cl}_4$: C, 38.47; H, 4.84. Found: C, 38.89; H, 4.99.

1-Bromo-1-methyl-2-(trichloromethyl)cyclohexane was prepared according to the literature procedure reported for the addition of BrCCl_3 to cyclohexene.^{16b} 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 ($\text{C}_8\text{H}_{12}\text{Cl}_3$) 179, 177, 143, 141, 109, 105, 95, 55, and 41. Bp 100–105 °C/0.2 mmHg. Attempts to isolate the product showed it to be thermally unstable (–HBr), since it was always contaminated with small amounts of olefin. ^1H NMR (CDCl_3 , 200 MHz): δ 1.38–1.78 (m, 4H), 1.84 (s, 3H, CH_3), 1.88–2.52 (m, 4H), 2.97 (m, ^1H) ppm. IR (gas phase): ν 2943, 2876, 1454, 1388, 1251, 1128, 929, 885, 777 (st), 648 cm^{-1} . EI^+ (GC/MS, VG-70): m/z 217, 215, 213 ($\text{M}^+ - \text{Br}$), 179, 177, 143, 141, 109, 105, 95, 55, 41. The 1,2-addition product was characterized by heating it to 150 °C and distilling to products, a mixture (1:0.20:0.28) of three olefinic products, bp 76 °C/1–1.25 mmHg: 1-methyl-2-(trichloromethyl)cyclohexene, 1-methylene-2-(trichloromethyl)cyclohexane, and 1-methyl-6-(trichloromethyl)cyclohexene. A microanalysis (GC/MS) of the isomeric mixture was consistent with its assignment. EI^+ (GC/MS, VG-70): m/z 212.0, 214.0, 216.0 (M^+), 163.0, 165.0, 167.0, 95.0, 67.0, 41.0; m/z 212.0, 214.0, 216.0 (M^+), 141.1, 95.0, 67.0 41.0; m/z 212.0, 214.0, 216.0 (M^+), 141.1, 95.1, 81.0, 67.0, 41.0. Anal. Calcd for $\text{C}_8\text{H}_{11}\text{Cl}_3$: C, 45.00; H, 5.19. Found: C, 45.12; H, 5.39.

1,1-Dichloro-2-hexylcyclopropane was prepared according to the literature procedure¹⁷ and identified by its GC/MS, GC/IR, ^1H NMR, ^{13}C NMR, and APT: ^1H 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^+ , $\text{C}_9\text{H}_{12}\text{Cl}_2$), 166, 152, 138, 123, 102, 83, 70, 56, and 41.

1-Chloro-1-methylcyclohexane was prepared according to the literature procedure.¹⁸ Distillation gave 1.1 g (81%) of 1-chloro-1-methylcyclohexane: bp 30–31 °C/6 mmHg (lit.¹⁷ bp 65.2–65.5 °C/44 mmHg); ^{13}C NMR (300 MHz, CDCl_3) δ 23.89 (q, 1H), 23.01, 25.23, 30.03, 41.58 (t, 5H), 72.00 (s, 1H); 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.

1,1,1-Trichloro-3-bromononane was prepared by the peroxide-catalyzed (Bz_2O_2) of BrCCl_4 (100 °C) in a 50% yield: bp 90–92 °C, 0.4 mmHg (lit.¹⁸ bp 99–102 °C at 0.6 mmHg); $\eta^{25}_{\text{D}} = 1.4926$ (lit.¹⁸ $\eta^{20}_{\text{D}} = 1.4943$); ^1H NMR (CDCl_3 , 200 MHz) δ 0.85 (t, 3H, $J = 7.0$ Hz), 1.25–1.60 (m, 8H), 1.85–2.10 (m, 2H), 3.12–3.25 (dd, 1H, $J = 4.0$ Hz, $J = 16$ Hz), 3.35–3.50 (dd, 1H, $J = 4.0$ Hz, $J = 16$ Hz), 4.25–4.40 (m, 1H).

1,1-Dichloro-2-butylcyclopropane was synthesized by the addition of dichlorocarbene to hexene:¹⁷ yield 55%, bp 60

°C/4 mmHg; ^1H NMR (200 MHz, CDCl_3) δ 1.00 (t, 3H, $J = 6.8$ Hz), 1.10 (m, 1H), 1.25–1.65 (m, 8H); EI^+ (GC/MS) m/z 165.9, 167.9, 169.9. Anal. Calcd for $\text{C}_7\text{H}_{12}\text{Cl}_2$: C, 5032; H, 7.24. Found: C, 50.00; H, 7.51. High resolution MS for $\text{C}_7\text{H}_{12}\text{Cl}_2^{35}$: $\text{C}_7\text{H}_{12}\text{Cl}_2^{35}$: calcd for 166.03160, found 166.03166.

1,1,1,3-Tetrachloroheptane was synthesized by the peroxide-catalyzed addition of CCl_4 to 1-hexene:^{16a} yield 36.1%; bp 58–60 °C/0.3 mmHg. ^1H NMR (200 MHz, CDCl_3) δ 0.95 (t, 3H, $J = 6.7$ Hz), 1.30–2.02 (m, 6H), 3.08–3.35 (AB, oct, 2H); 4.27 (sext, 1H, $J = 5.0$ Hz); EI^+ (GC/MS) m/z 236.0, 238.0, 240.0 (M^+). Anal. Calcd for $\text{C}_7\text{H}_{12}\text{Cl}_4$: C, 35.33; H, 5.07. Found: C, 35.07; H, 4.97.

2-Chlorohexane was prepared by the reactions of 2-hexanol with thionyl chloride and pyridine using the method of Brooks and Snyder:¹⁹ yield 53%, bp 123 °C (lit.²⁰ 123 °C); EI^+ m/z 120.0, 122.0 (M^+).

1,1,1,3-Tetrachlorononane. The addition product was prepared according to the literature method by the peroxide catalyzed addition of CCl_4 to 1-octene:^{16a} yield 70.3%, bp 94 °C/0.2 mmHg (lit.^{16a} bp 78–79 °C/0.1 mmHg); $\eta^{20}_{\text{D}} = 1.47675$ (lit.¹⁴ $\eta^{20}_{\text{D}} = 1.4770$). The ^1H NMR [(200 MHz, CDCl_3) δ 0.91 (t, 3H, $J = 6.7$ Hz), 1.30–2.0 (m, 10H), 3.08, 3.10, 3.16, 3.18, 3.24, 3.27, 3.32, 3.35 (AB, 8 peaks, 2H), 4.25 (6 peaks), 1H, $J = 5.0$ Hz)] was consistent with the 60 MHz spectra reported by Burton and Kehoe.²¹

cis- and trans-2-hexene were prepared as a mixture with 1-hexene from 2-hexanol and H_2SO_4 (5.8:5.7:1). The products were identified by a comparison of their GC/IR²² and GC/MS with those of the authentic materials. EI^+ m/z 84 (M^+).

dl- and meso-5,6-dimethyldecane (1:1) and 5-methylundecane were prepared as a mixture by allowing neat 1-hexene to react with atomic hydrogen^{2,3} at –78 °C. The products were identified by their GC/MS and the ^1H NMR of the mixture. The isomeric mixture was isolated by distillation, and a microanalysis of the mixture was obtained. Anal. Calcd for $\text{C}_{12}\text{H}_{26}$: C, 84.61; H, 15.39. Found: C, 84.55; H, 15.44. The ^1H NMR of the methyl protons δ 0.94–0.71 were in the same ratio as the absorption and chemical shift positions as was found in the corresponding products reported for 1-octene.²

1-Bromo-1-methylcyclohexane was prepared from 1-methylcyclohexene (0.050 mol, 4.80 g) and 50 mL of aqueous 48% HBr. The reaction mixture was stirred under an atmosphere of N_2 for 2 days at 45 °C. The solution was extracted with hexane, washed with H_2O , dried over anhydrous MgSO_4 , and filtered, and the filtrate was distilled under vacuum, bp 45–46 °C/4 mmHg; $\eta^{25}_{\text{D}} = 1.4496$ (lit.²³ bp 66.0–66.5/22 mmHg; $\eta^{25}_{\text{D}} = 1.4468$). Yield 5.31 g (68.7%) of the product 1-bromo-1-methylcyclohexane. ^1H NMR (CDCl_3 , 200 MHz) δ 2.00–2.14 (m, 4H, 2- CH_2), 1.82 (s, 3H, CH_3), 1.40–1.78 (m, 6H, 3 CH_2). Anal. Calcd for $\text{C}_7\text{H}_{13}\text{Br}$: C, 47.48; H, 7.40. Found: C, 47.41; H, 7.62.

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