

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

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**Abstract:** The solution-phase reactions of microwave-generated hydrogen atoms with terminal olefins is regioselective. Since addition is to the terminal end of the olefin, the reaction yields a secondary radical which undergoes either reaction with molecular or atomic hydrogen, disproportionation, combination, or addition to another olefin, and in the case of hydrogen atom addition to 1,6-heptadiene, cyclization. The cyclized radicals are formed reversibly, and the final product mixture contains only minor amounts of *cis*-1,2-dimethylcyclopentane (the product of kinetic control) while the major cyclized product is methylcyclohexane. Although an equilibrium mixture could not be obtained, the dimethylcyclopentyl and 3-methylcyclohexyl radicals were shown to be formed reversibly.

## Introduction

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

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.<sup>34</sup> In a preliminary report on the addition of hydrogen atoms generated by microwave discharge to a number of olefins,<sup>35</sup> 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,<sup>35</sup> hydrogen atoms generated in a microwave discharge are passed over a stirred solution of the reactive substrate. The products formed in these highly chemospecific reactions are analyzed, and the solution-phase structure–reactivity relationships for the reactions of atomic hydrogen are obtained.

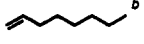

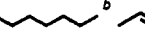

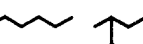
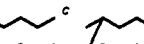
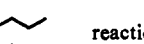
**Regioselective Addition.** When atomic hydrogen (0.70–4.44 mmol) is passed over neat 1-octene (–78 °C) the products of the reaction are octane, *cis*- and *trans*-2-octene, and two structurally different dimeric products (*meso*- and *d,l*-7,8-dimethyltetradecane and 7-methylpentadecane), see Table 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 distributions of the products from these reactions are listed in Table 2. By comparing the mass and <sup>1</sup>H and <sup>2</sup>H NMR spectra of the protiated to deuterated products of the reaction mixture, it is obvious that in each of the products, monomers or dimers, at least one deuterium is attached to a terminal position attributable to the original olefin, see Table 2: The mass spectra of the products show 1-octene (*d*<sub>0</sub> and *d*<sub>1</sub> (A)), octane (*d*<sub>1</sub> (B) and *d*<sub>2</sub> (C)), *trans*-2-octene (*d*<sub>1</sub> (D)), *cis*-2-octene (*d*<sub>1</sub> (E)), 7,8-dimethyltetradecane (*d*<sub>2</sub> (F)), and 7-methylpentadecane (*d*<sub>2</sub> (G)). If the assumption is correct that the

- \* Abstract published in *Advance ACS Abstracts*, June 15, 1994.
- (1) Jennings, K. R.; Cveticanovic, R. J. *J. Chem. Phys.* 1961, 35, 1233.
  - (2) Michael, J. V.; Weston, R. E., Jr. *J. Chem. Phys.* 1966, 45, 3632.
  - (3) Braun, W.; Lenzi, M. *Discuss. Faraday Soc.* 1967, 44, 252.
  - (4) Eyre, J. A.; Hikida, T.; Dorfman, L. M. *J. Chem. Phys.* 1970, 53, 1281.
  - (5) Kurylo, M. J.; Peterson, N. C.; Braun, W. *J. Chem. Phys.* 1970, 53, 2776.
  - (6) Cowfer, J. A.; Keil, D. G.; Michael, J. V.; Yeh, C. *J. Phys. Chem.* 1971, 75, 1584.
  - (7) Penzhorn, R. D.; de B. Darwent, B. *J. Chem. Phys.* 1971, 55, 1508.
  - (8) Teng, L.; Jones, W. E. *J. Chem. Soc., Faraday Trans. 1* 1972, 68, 1267.
  - (9) Cveticanovic, R. J.; Doyle, L. C. *J. Chem. Phys.* 1969, 50, 4705.
  - (10) Woolley, G. R.; Cveticanovic, R. J. *J. Chem. Phys.* 1969, 50, 4697.
  - (11) Yang, K. *J. Am. Chem. Soc.* 1962, 84, 719.
  - (12) Yang, K. *J. Am. Chem. Soc.* 1962, 84, 3795.
  - (13) Allen, P. E. M.; Melville, H. W.; Robb, J. C. *Proc. R. Soc. London, A* 1953, 218, 311.
  - (14) Bradley, J. N.; Melville, H. W.; Robb, J. C. *Proc. R. Soc. London, A* 1956, 236, 318.
  - (15) Daby, E. E.; Niki, H.; Weinstock, B. *J. Phys. Chem.* 1971, 75, 1601.
  - (16) Oka, K.; Cveticanovic, R. J. *Can. J. Chem.* 1979, 57, 777.
  - (17) Muedas, C. A.; Ferguson, R. R.; Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* 1991, 113, 2233.
  - (18) Gebhardt, J.; Scherzer, K. *J. Prakt. Chem.* 1988, 330, 853.
  - (19) Scherzer, K.; Gebhardt, J.; Olzmann, M. *Ber. Bunsen-Ges. Phys. Chem.* 1990, 94, 1265.
  - (20) Gebhardt, J.; Scherzer, K. *J. Prakt. Chem.* 1991, 333, 313.
  - (21) Rabinovitch, B. S.; Setser, D. W. *Adv. Photochem.* 1964, 3, 1.
  - (22) Falconer, W. E.; Sunder, W. A. *Int. J. Chem. Kinet.* 1972, 4, 315.
  - (23) Bradley, J. N.; Melville, H. W.; Robb, J. C. *Proc. R. Soc. London, A* 1956, 236, 454.
  - (24) Takahashi, M.; Cveticanovic, R. J. *Can. J. Chem.* 1962, 40, 1037.
  - (25) Scheer, M. D.; Klein, R. *J. Phys. Chem.* 1959, 63, 1517.
  - (26) Scheer, M. D.; Klein, R. *J. Phys. Chem.* 1961, 65, 375.
  - (27) Boddy, P. J.; Robb, J. C. *Proc. R. Soc. London, A* 1959, 249, 518.

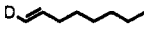
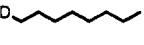
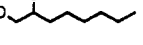
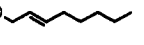
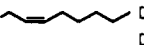
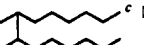
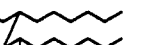
- (28) Bradley, J. N.; Melville, H. W.; Robb, J. C. *Proc. R. Soc. London, A* 1956, 236, 339.
- (29) Moore, W. J. *J. Chem. Phys.* 1948, 16, 916.
- (30) Moore, W. J.; Wall, L. A. *J. Chem. Phys.* 1949, 17, 1325.
- (31) Harrington, R. E.; Rabinovitch, B. S.; Frey, H. M. *J. Chem. Phys.* 1960, 33, 1271.
- (32) Cveticanovic, R. J. *Adv. Photochem.* 1963, 1, 158.
- (33) Kelley, R. D.; Klein, R.; Scheer, M. D. *J. Phys. Chem.* 1965, 69, 905.
- (34) Hardwick, T. J. *J. Phys. Chem.* 1962, 66, 291.
- (35) Beeri, A.; Berman, E.; Vishkautsan, R.; Mazur, Y. *J. Am. Chem. Soc.* 1986, 108, 6413.

Table 1. Product Distribution of the Addition of Atomic Hydrogen to 1-Octene

reaction %	H <sup>•</sup> (mmol) <sup>a</sup>								reaction time (min)
1.10	0.70	20.70	18.04	33.76	10.44	2.62	13.29	1.17	4
2.10	1.33	20.27	20.49	32.78	10.14	2.37	12.91	1.04	7
3.09	1.96	16.38	27.70	29.82	10.90	2.54	11.74	0.92	11
7.00	4.44	12.76	28.60	30.69	13.08	2.76	11.26	1.18	25

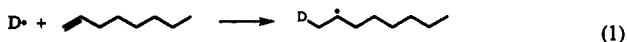
<sup>a</sup> H<sub>2</sub> flow rate of 4 mL/min. <sup>b</sup> Calculated using the data from Table 2. Products formed by the disproportionation reaction. <sup>c</sup> A 1:1 mixture of *meso*- and *d,l*-dimers.

Table 2. Product Distribution of the Addition of Deuterium Atoms to 1-Octene (-78 °C)<sup>a,b</sup>

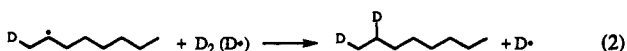
reaction %	[olefin]								$\rho_{MDA}/\rho_{MDE}$	$k_d/k_c$
4.40	6.38	17.14	30.84	26.91	9.07	2.80	11.81	1.44	1.06	2.61
8.05	1.07	22.28	34.86	14.18	11.04	2.33	14.46	0.85	0.91	2.56
18.80	0.70	23.83	34.31	12.97	11.28	2.53	13.39	1.69	0.91	2.56
35.64	6.38	16.83	32.58	23.15	11.17	2.43	12.68	1.19	1.07	2.57
								average	1.00	2.45

<sup>a</sup> Concentrations (23 °C) were neat (6.38 M) 1-octene or solution in acetone. <sup>b</sup> The product distribution was calculated using the data obtained from GC and <sup>2</sup>H NMR analyses. <sup>c</sup> A 1:1 mixture of *meso*- and *d,l*-dimers.

initial reaction is regiospecific addition to the terminal position of 1-octene, then the deuterated products are those listed in Table 2. The <sup>2</sup>H NMR spectra show absorptions with intensities ( $I_n$ ) at  $\delta$  1.00 (DCH<sub>2</sub>-,  $I_1$ ), 1.40 (-CDH-,  $I_2$ ), 1.65 (DCH<sub>2</sub>-CH=C-,  $I_3$ ), and 5.10 (DCH=H-,  $I_4$ ). From the concentrations of the products, the distribution of the deuterated products is calculated, see Table 2. The proportionality constant,  $f$ , is obtained from the equation  $I_3 = ([D] + [E])/f$ , and the unknown product concentrations are obtained from 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).

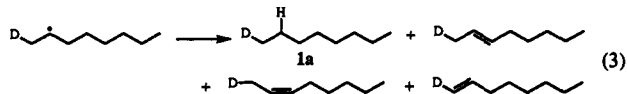


When the secondary radical encounters deuterium atom or a molecule of deuterium, 1,2-dideuteriooctane is formed (eq 2).<sup>36</sup> The species involved in the bimolecular reaction which caps the



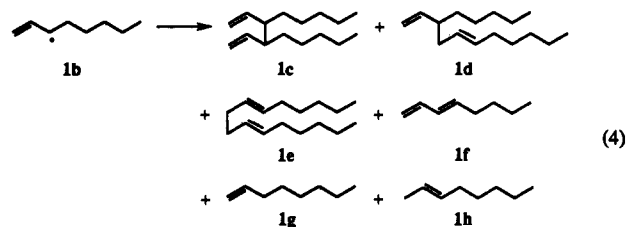
secondary radical, either D<sub>2</sub> or D<sup>•</sup> (eq 2), can not be unequivocally assigned since, using the vapor-phase literature values for the activation parameters for both of these reactions, both reactions at -78 °C appear to be prohibitively slow.<sup>36</sup>

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



observation that the ratio of mono-deuterated octane to octenes ( $\rho_{MDA}/\rho_{MDE}$ ) 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 molecular deuterium; however, the 1/1 ratio,  $\rho_{MDA}/\rho_{MDE}$ , 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 or no (<10%)

allylic abstraction (the most labile hydrogen) takes place.<sup>37</sup> If allylic abstraction accounts for the formation of **1a**, then products (disproportionation and combination) from the reaction of the allylic radical **1b** will also be observed (eq 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 conversion (4–26% reaction) is  $2.54 \pm 0.07$  (-78 °C). When the reaction is carried out at several temperatures, -100 °C, -78 °C, and -42 °C, a plot of  $\ln k_d/k_c$  vs  $1/T$  gives a slope,  $E_{a(\text{dis})} - E_{a(\text{comb})}$ , equal to 1.0 kcal/mol (see Figure 1). The ratio of rate constants,  $k_d/k_c$ , calculated from the plot at 25 °C is 1.01 and is identical to the value ( $k_d/k_c = 1.0, 1.1$ ) reported for the *sec*-butyl radical.<sup>41a</sup>

(36) The rate constant for the addition of atomic hydrogen to an olefin has been reported as approximately  $10^9$  L mol<sup>-1</sup> s<sup>-1</sup> both in the vapor phase<sup>37</sup> and in aqueous solution.<sup>38</sup> Since the reaction of H<sup>•</sup> with neat 1-octene (6.383 M) yielded a 1.1% conversion in 4 min, the concentration of [H<sup>•</sup>] can be estimated as  $\approx 10^{-14}$  M:  $\Delta P/\Delta t = k[\text{H}^\bullet][1\text{-octene}]^0$ . The diffusion-controlled reaction,  $k \approx 10^{10}$  L mol<sup>-1</sup> s<sup>-1</sup>, between the secondary radical,  $[\text{R}^\bullet] \approx 10^{-9}$  M, and a hydrogen atom,  $[\text{H}^\bullet] \approx 10^{-14}$  M, would apparently be too slow to account for the amount of saturated product formed. However, using the vapor-phase activation parameters to calculate the rate constant at -78 °C for the reaction of a methyl radical with molecular hydrogen,<sup>9</sup>  $k^{-78^\circ\text{C}} = 7.0 \times 10^{-5}$  M<sup>-1</sup> s<sup>-1</sup>, and the approximate concentrations of a saturated solution of hydrogen in a hydrocarbon at this temperature (0.04 M),<sup>40</sup> the rate of  $(7.0 \times 10^{-5})[0.04][10^{-9}] = 2.8 \times 10^{-15}$  L mol<sup>-1</sup> s<sup>-1</sup> would also be prohibitively slow. No doubt this anomaly is due to the inappropriate use of the reported addition reaction rates to account for the solution-phase reactions.

(37) Jones, W. E.; Macknight, S. D.; Teng, L. *Chem. Rev.* 1973, 73, 407.

(38) Neta, P. *Chem. Rev.* 1972, 72, 533.

(39) Walker, R. W. *J. Chem. Soc. A* 1968, 2391.

(40) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds*; Macmillan: New York, 1963; Vol. 1, Part 1, p 542.

(41) (a) Gibian, M. J.; Corley, R. C. *Chem. Rev.* 1973, 73, 448. (b) Schuh, H.; Fischer, H. *Helv. Chem. Acta* 1973, 61, 2463. (c) Tanner, D. D.; Rahimi, P. M. *J. Am. Chem. Soc.* 1982, 104, 225.

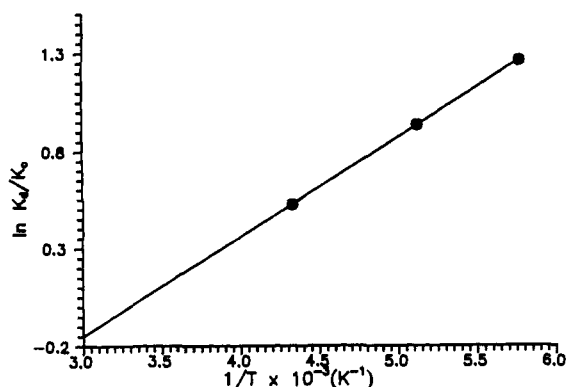
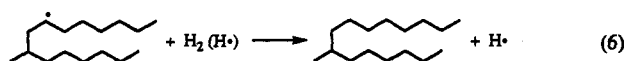
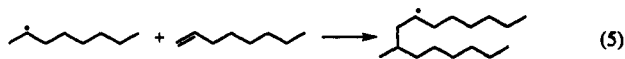


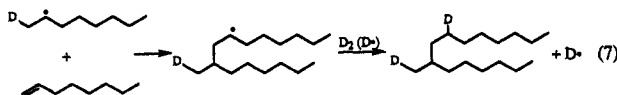
Figure 1. Plot of  $\ln k_d/k_c$  vs  $1/T$  for the self reactions of 1-methylheptyl radicals.

The ratio of rate constants,  $k_d/k_c$ , changes with temperature, predictably to smaller values as the temperature is increased, since at lower temperatures (*i.e.*, higher viscosity) molecular rotation is disfavored as is the rate for the disproportionation reaction.<sup>41b,c</sup> 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 are formed from disproportionation when the reaction of 1-octene and hydrogen atoms is carried out (see Table 1, footnote b). The yield of the dimeric product, 7-methylpentadecane, was shown to be dependent upon the initial concentration of olefin, see Table 3.

The concentration dependence of the yield of 7-methylpentadecane is consistent with its formation from a bimolecular reaction and must be due to addition of the 1-methylheptyl radical to the terminal position of 1-octene (eq 5), followed by subsequent transfer of the new secondary radical with hydrogen (eq 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 to contain deuterium at the 7-methyl and on the 9-position of the pentadecane, see eq 7. Both the concentration dependence of the addition dimer and its deuterium substitution pattern clearly establish its formation mechanism.



**Reversible Radical Cyclization.** During the last 25 years, since it was first reported,<sup>42</sup> the ring closure reactions of the 5-hexenyl radical and its substituted analogs by intramolecular addition have been extensively investigated.<sup>43-52</sup> The cyclizations to give five-membered rings have been widely accepted as a mechanistic

(42) Arai, S.; Sato, S.; Shida, S. *J. Chem. Phys.* **1960**, *33*, 1277.

(43) Lamb, R. C.; Ayers, P. W.; Toney, M. K. *J. Am. Chem. Soc.* **1963**, *85*, 3483.

(44) (a) Julia, M.; Le Goffie, F. C. *R. Hebd. Seances Acad. Sci.* **1962**, *255*, 714. (b) Julia, M.; Maumy, M. *Bull. Soc. Chim. Fr.* **1966**, 434. (c) Julia, M.; Maumy, M. *Bull. Soc. Chim. Fr.* **1966**, 2321. (d) Julia, M.; Maumy, M.; Mion, L. *Bull. Soc. Chim. Fr.* **1967**, 2641.

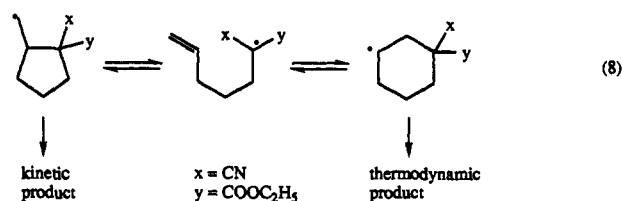
(45) (a) Walling, C.; Pearson, M. S. *J. Am. Chem. Soc.* **1964**, *86*, 2262. (b) Walling, C.; Cooley, J. H.; Ponnaras, A. A.; Racah, E. J. *J. Am. Chem. Soc.* **1966**, *88*, 5361. (c) Walling, C.; Cioffai, A. *J. Am. Chem. Soc.* **1972**, *94*, 6059.

probe which is characteristic of a free radical intermediate<sup>53-55</sup> and have been used as a standard for the determination of the absolute rates of a wide variety of competitive free radical reactions.<sup>56-58</sup>

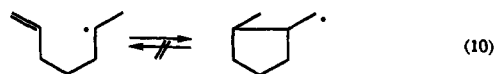
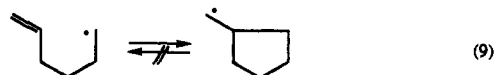
With an understanding of the mechanism of these cyclization reactions, their use as standard synthetic methodology has rapidly been established.<sup>59-62</sup>

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 (0.02–0.5 M) in order to sustain the chain reaction and to achieve isolatable yields.<sup>45c</sup>

The literature contains examples of radical cyclizations which form six-membered rings when the radical center is stabilized by substitution.<sup>44</sup> The stabilized radical closes and opens reversibly and eventually yields the thermodynamically more stable six-membered carbocyclic radical, which in turn in a nonchain process yields the thermodynamically more stable product (eq 8). During



the thermal decomposition of pentenylacetyl peroxide, another nonchain process, the radical cyclization appears to be reversible since a substantial amount of six-membered ring hydrocarbon was formed.<sup>43</sup> 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 six-membered ring hydrocarbon was formed,<sup>45c</sup> however, under the conditions used to follow the kinetics of the reaction, the five-membered ring was shown to be irreversibly formed (eqs 9 and 10). Although



it was not shown to be formed irreversibly, the radical from a disubstituted olefin also cyclizes to yield six-membered ring

(46) Garwood, R. G.; Scott, C. J.; Weedon, B. C. L. *Chem. Commun.* **1965**, *1*, 14.

(47) (a) Brace, N. O. *J. Org. Chem.* **1966**, *31*, 2879. (b) Brace, N. O. *J. Org. Chem.* **1967**, *32*, 2711.

(48) Beckwith, A. L. J.; Phillipou, G. J. *J. Am. Chem. Soc.* **1974**, *96*, 1613.

(49) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299.

(50) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground & Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1.

(51) Surzur, J. M. In *Reactive Intermediates*; Abramovitch, A. A., Ed.; Plenum Press: New York, 1981; Vol. 2, Chapter 3.

(52) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

(53) Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395.

(54) Garst, J. F.; Smith, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 1520.

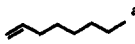
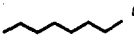
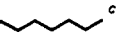
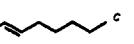
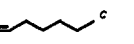
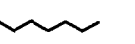
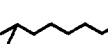
(55) (a) Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* **1984**, *49*, 3545. (b) Ashby, E. C.; Oswald, J. *J. Org. Chem.* **1988**, *53*, 6068. (c) Ashby, E. C.; Coleman, D. *J. Org. Chem.* **1987**, *52*, 4554. (d) Ashby, E. C.; Wenderoth, B.; Pham, T. N.; Park, W. S. *J. Org. Chem.* **1984**, *49*, 4505. (e) Ashby, E. C.; Bowers, J.; DePriest, R. *Tetrahedron Lett.* **1980**, *21*, 3541. (f) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545.

(56) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(57) (a) Lol, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355. (b) Schmid, P.; Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.* **1979**, *11*, 333. (c) Chatgililoglu, C.; Ingold, K. U.; Sciano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

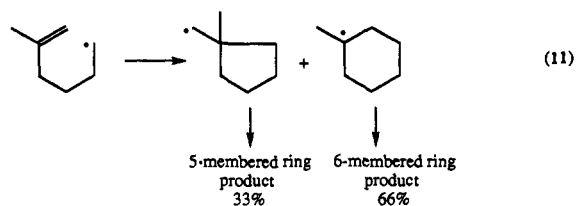
(58) Beckwith, A. L. J.; Cliff, M. D.; Schiesser, C. H. *Tetrahedron* **1992**, *48*, 4641.

Table 3. Products from the Reaction of Hydrogen Atoms with Acetone Solutions of 1-Octene

[olefin]	[1-octene] left (%)	 <sup>a</sup>	 <sup>b</sup>	 <sup>c</sup>	 <sup>c</sup>	 <sup>c</sup>	 (meso- and dl-, 1:1)	
0.007	20.34	(27.11)	(23.83)	(31.82)	4.71	tr	12.53	
0.014	22.08	(26.84)	(23.07)	(32.14)	5.30	tr	12.65	
0.145	74.84	(25.28)	(8.29)	(37.79)	10.37	2.14	14.88	1.25
0.216	64.34	(22.23)	(14.39)	(35.18)	10.83	2.12	3.85	1.40

<sup>a</sup> Calculated using  $k_d/k_c = 2.54$ ;  $\rho_{MDA}/\rho_{MDE} = 1$ . <sup>b</sup> Hydrogen addition-addition products. <sup>c</sup> Disproportionation products.

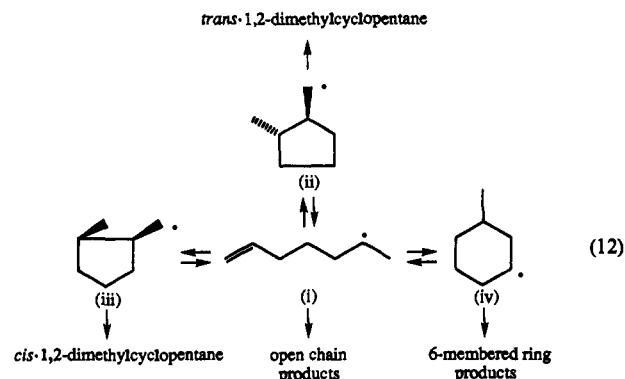
products (eq 11). Closure to the five-membered ring was presumably sterically disfavored.<sup>63</sup>



**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, five-/six-member ring, under conditions where the transfer reaction is extremely slow due to the low concentration of atomic hydrogen. Under these conditions ( $-78\text{ }^\circ\text{C}$ ,  $[\text{H}^\bullet] \approx 10^{-14}\text{ M}$ ),<sup>36</sup> 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 4–6. When either deuterium or protium atoms are used (Tables 4–6), it is clear that six-membered ring products,  $P_6$ , are formed in preference to the five-membered ring carbocycles,  $P_5$ . As the concentration of  $[\text{H}_2]$  was increased (Table 5), the ratio of products,  $P_6/P_5$ , decreased. Although closure to the *cis*-five-membered ring is kinetically favored, reversible cyclization favors the formation of the six-membered ring. At  $25\text{ }^\circ\text{C}$  the ratio of *cis*-/*trans*-1,2-dimethylcyclopentane is 73/27, and the activation parameters reported ( $E_{trans}^{\ddagger} - E_{cis}^{\ddagger} = 0.7\text{ kcal mol}^{-1}$ )<sup>63</sup> predict that at  $-78\text{ }^\circ\text{C}$  the products should be 58/42 = *cis*/*trans* for an irreversible cyclization. The reversible hydrogen atom promoted cyclization (Table 4) shows a 28/72 ratio at  $-78\text{ }^\circ\text{C}$ . At low concentrations of hydrogen, the cyclized radical has a longer lifetime and ring opening takes place. A plot of the hydrogen atom flux vs the ratio  $P_6/P_5$  extrapolates to 1.57 at a hydrogen atom concentration of zero. If the cyclization is truly reversible, an equilibrium distribution of products will eventually be established, see Scheme 1.

Unfortunately equilibrium cannot be reached since very fast,  $k \approx 10^9\text{ M}^{-1}\text{ s}^{-1}$ , bimolecular reactions (combination, disproportionation, and reactions with molecular hydrogen) 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  $\text{H}_2$ , see Table 5. When the hydrogenation is carried out to higher conversion (Table 4, reactions 2 and 3), the product mixture contains five-membered ring, six-membered ring, and open chained hydrocarbons. The

Scheme 1



dimeric products are derived from open chained radicals *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 mono-olefinic 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 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 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(deuteriomethyl)-1,11-dodecadiene, see Table 6. The distribution of deuterium in the product mixture can be obtained by analysis of its mass spectra, GC integration, and  $^1\text{H}$  and  $^2\text{H}$  NMR.

The mass spectra (GC/MS) of the products showed the following: 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)), 3-methylcyclohexene ( $d_1$  (Q)), 4-methylcyclohexene ( $d_1$  (P)), and 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 regioselective 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 6. The  $^2\text{H}$  NMR showed absorption with intensity,  $I_n$ :  $\delta$  1.00 (DCH<sub>2</sub>-,  $I_1$ ), 1.40 (-DCH-,  $I_2$ ), 1.65 (DCH<sub>2</sub>-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,  $f$ , is obtained from the equation  $I_3 = [\text{K}]/f$ . Using the relationships  $[\text{H}] = fI_1$ ,  $[\text{J}] = fI_2 - [\text{O}]$ , and  $[\text{S}] = fI_1 - 2[\text{L} + \text{M} + \text{R}] - fI_2 - [\text{N} + \text{P} + \text{Q}]$ , the distribution of mono-deuterated products is obtained.

It is not obvious, however, that the six-membered ring radical, iv, is in fact reversibly formed. To test the assumption that iv is formed reversibly, advantage is taken of a previously made observation that alkyl bromides are dehalogenated during their

(59) Mehta, G.; Murthy, A. N.; Reddy, D. S.; Reddy, A. V. *J. Am. Chem. Soc.* 1986, 108, 3443.

(60) Hart, D. J.; Huang, H. C.; Krishnamurthy, R.; Schwartz, T. J. *J. Am. Chem. Soc.* 1989, 111, 7507.

(61) (a) Curran, D. P.; Chen, M. H.; Kim, D. *J. Am. Chem. Soc.* 1989, 111, 6265. (b) Curran, D. P.; Abraham, A. C.; Liu, H. J. *J. Org. Chem.* 1991, 56, 4335. (c) Curran, D. P.; Kim, D. *Tetrahedron* 1991, 47, 6171.

(62) Bachi, M. D.; Denenmaek, D. *J. Org. Chem.* 1990, 55, 3442.

(63) (a) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* 1985, 41, 3925.

(b) Beckwith, A. L. J.; Meijis, G. F. *J. Chem. Soc., Perkin Trans. 2* 1979, 1535. (c) Beckwith, A. L. J.; Phillipou, G.; Serelis, A. K. *Tetrahedron Lett.* 1981, 22, 2811.

Table 4. Reaction Products of 1,6-Heptadiene with Atomic Hydrogen<sup>a</sup>

run	products (% yield) <sup>b</sup>														P <sub>6</sub> / P <sub>5</sub> <sup>c</sup>	
																other dimers
1	95.02	0.56	2.00	0.58				0.21	0.82			0.20	0.61			1.33
2	76.97	2.02	8.92	2.37	1.67	tr	tr	0.67	2.68	tr		0.82	2.92	0.60	0.35	1.30
3	49.32	4.40	16.31	4.37	6.53	1.89	0.72	1.66	5.82	tr		1.58	3.76	2.52	1.12	1.22
4	00.00		0.0	0.0		0.0	0.0					0.0	0.0	(1:0.97) <sup>d</sup>	(0.09) <sup>d</sup>	

<sup>a</sup> [1,6-Heptadiene] = 0.0740 M in acetone. <sup>b</sup> Seven dimeric products were detected: two diene coupling products (*meso*- and *dl*-); 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. <sup>c</sup> The ratio of six- to five-membered-ring cyclized products. <sup>d</sup> The dimeric products consisted of >97% *meso*- and *dl*-6,7-dimethyldodecane and 6-methyltridecane (1:0.97:0.09).

Table 5. Reaction products of 1,6-Heptadiene with Atomic Hydrogen<sup>a</sup>

H <sub>2</sub> flow rate (mL/min)	products (% yield)														P <sub>6</sub> / P <sub>5</sub> <sup>c</sup>
4/3.5 <sup>d</sup>	80.11	1.24	6.57	2.36	1.59	0.48	0.23	0.81	2.20	0.17	0.77	1.92	0.57	0.98	1.45
20 <sup>e</sup>	53.87	4.71	11.86	4.01	5.88	1.58	0.74	2.10	5.90	0.28	1.84	3.70	1.88	1.67	1.10

<sup>a</sup> Concentration in acetone (0.1035 M). <sup>b</sup> Other dimers, see Table 4. <sup>c</sup> The ratio of six-/five-membered-ring cyclized products. <sup>d</sup> 4 mL/min of H<sub>2</sub> (3.5 min). <sup>e</sup> 20 mL/min of H<sub>2</sub> (1.5 min).

Table 6. Reaction of Deuterium with 1,6-Heptadiene<sup>a-c</sup>

	product %	proposed mechanism
H	12.46	D atom addition-disproportionation
S	26.27	D atom addition-disproportionation
J	8.75	D atom addition-D atom addition
K	11.42	D atom addition-disproportionation
		( <i>trans</i> - + <i>cis</i> -)
L	6.02	D atom addition-cyclization-D atom addition
M	5.33	D atom addition-cyclization-D atom addition
N	3.90	D atom addition-cyclization-disproportionation
O	6.97	D atom addition-cyclization-D atom addition
P,Q	5.76	D atom addition-cyclization-disproportionation
R	13.11	D atom addition-combination
		( <i>d,l</i> - and <i>meso</i> -, 1:1)

<sup>a</sup> Concentration in acetone (0.16 M). <sup>b</sup> Conversion = 3.1%. <sup>c</sup> P<sub>6</sub>/P<sub>5</sub> = 1.46, ρ<sub>MDA</sub>/ρ<sub>MDO</sub> = 1.02, k<sub>d</sub>/k<sub>c</sub> = 2.30 (-78 °C).

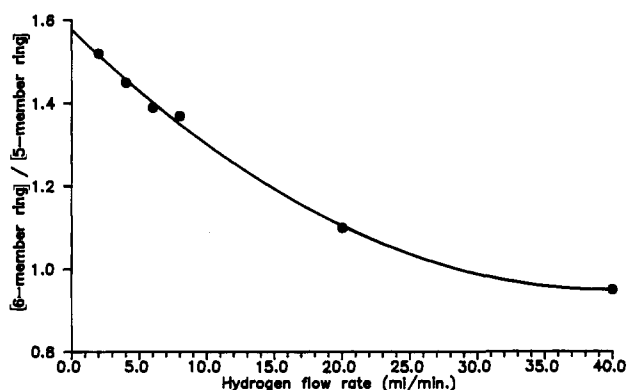


Figure 2. Plot of the hydrogen atom flow rate vs the ratio of six-/five-membered ring products.

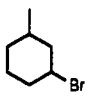

reaction with atomic hydrogen (eq 13).<sup>64</sup> When 1-methyl-3-



bromocyclohexane is allowed to react with atomic hydrogen, it forms among other products heptane (see Table 7). The formation of the saturated alkane via radical *i* is expected since  $k_{\text{addition}} \gg$

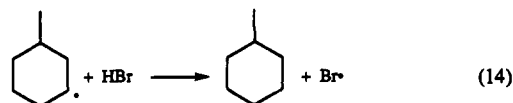
(64) Unpublished results from this laboratory.

Table 7. Hydrogen-Promoted Ring-Opening Reactions of the 3-Methylcyclohexyl Radical

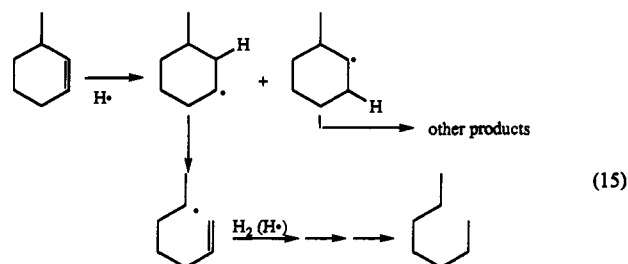
substrate	products (yield, %)	SM (%)
	heptane (3.1) methylcyclohexane (55.9) dimer (19.8)	21.5
	heptane (0.14) methylcyclohexane (47.9) dimer (51.6)	0.37

<sup>a</sup> 1.1 M in acetone, H<sub>2</sub> (20 cc/min), 60 min. <sup>b</sup> 0.2 M in acetone, H<sub>2</sub> (2 cc/min), 60 min.

$k_{\text{abstraction}}$  (i.e., for abstraction of either a bromine atom or a hydrogen atom).<sup>64</sup> 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 7). The 3-methylcyclohexenyl



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



**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<sup>-7</sup> mol/L. This secondary radical either reacts with a hydrogen atom or molecular 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 radicals cyclize to the more stable *trans*-five- and -six-membered ring radicals, see eq 12. Although the radical intermediates are all reversibly formed, the equilibrium mixture of products is never reached since subsequent fast reactions no doubt remove the intermediates from the reaction media.

### Experimental Section

**General Method for the H Atom Reactions.** The substrate was placed in the Pyrex reactor and cooled to -78 °C. Helium and hydrogen or deuterium were introduced into the system at the desired flow rate, and the pressure of the system was maintained at 3–4 Torr. The H<sub>2</sub>-He plasma was generated in the microwave cavity, and the hydrogen atoms were swept over the stirred solution.

**Instrumentation.** The <sup>1</sup>H, <sup>2</sup>H, and <sup>13</sup>C NMR spectra were obtained using either a Bruker AM-400 (400 MHz), Bruker AM-300 (300 MHz) or Bruker WH-200 (200 MHz) NMR spectrometer. Unless otherwise noted the <sup>1</sup>H NMR spectra are referenced to TMS as an internal standard at 0.00 ppm or CHCl<sub>3</sub> as an internal standard at 7.26 ppm. The <sup>13</sup>C NMR chemical shifts are reported in δ (ppm) relative to chloroform (δ CDCl<sub>3</sub> = 77.0). The <sup>13</sup>C spectra were studied by APT (attached proton test) to determine the number of protons attached to each carbon.

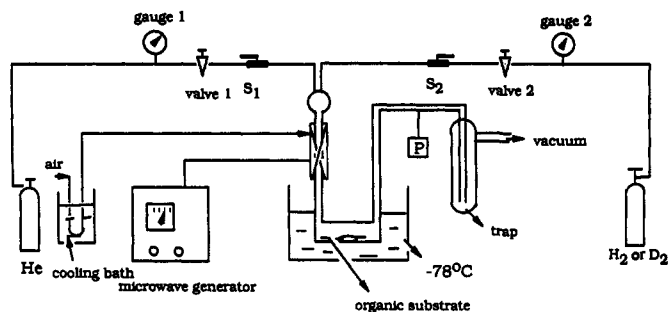


Figure 3. Diagram of apparatus for H atom reactions.

GC/IR data were obtained using a HP 5965A IRD GC/FTIR interfaced to a HP 5890 gas chromatograph fitted with a DB-5 (30 m  $\times$  0.25 mm) glass capillary column.

GC/MS data were obtained using a VG-70E EI<sup>+</sup> spectrometer fitted with a Varian Vista 6000 gas chromatograph having a glass capillary column (DB-5, 30 m  $\times$  0.25 mm, J. & W. Scientific) and interfaced to a 1125 data system.

GC analyses were carried out using a Varian Vista 6000, FID, gas chromatograph fitted with a glass capillary column (PONA, 30 m  $\times$  0.25 mm, Hewlett Packard) and interfaced to a Varian Vista CDS 401 chromatographic data system. The yield of the reaction products was determined by GC analysis using a standard calibration solution of known concentrations of the authentic materials and an added internal standard (1-chlorooctane or *o*-dichlorobenzene).<sup>65</sup>

The products were identified by a comparison of their GC retention times, GC/IR spectra, and GC/MS spectra with those of authentic samples (in the cases of *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 (1:1) was obtained by preparative GC (100 °C, 10 ft  $\times$  1/4-in. SE-30 column) from the product mixture resulting from the addition of atomic hydrogen to 1-octene. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.73 (d, 3H), 0.82 (d, 3H), 0.89 (t, 6H), 1.27 (m, 22H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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*-). An APT spectrum was consistent with the above assignments. The mass spectra had a molecular ion, C<sub>16</sub>H<sub>34</sub>, at  $m/z^+$  226.

7-Methylpentadecane was prepared according to the literature procedure from the cuprate of 2-octyllithium and 1-bromooctane.<sup>66</sup> <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>):  $\delta$  0.84 (d, 3H), 0.89 (t, 6H), 1.27 (m, 25H). The mass spectra had a molecular ion, C<sub>16</sub>H<sub>34</sub>, at  $m/z^+$  226.

*trans*- and *cis*-1,2-Dimethylcyclopentane were obtained by the reactions of 6-bromo-1-heptene with tributyltin hydride.<sup>66</sup> 6-Bromo-1-heptene was prepared according to the literature procedure.<sup>45c</sup> bp 79 °C (20 mmHg); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  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  $\nu$  3080, 2960, 1640, 1440, 1375 cm<sup>-1</sup>. *trans*- and *cis*-1,2-Dimethylcyclopentane in the product mixture from the addition of atomic hydrogen to 1,6-heptadiene were identified by their mass spectral cracking patterns (GC/MS<sup>69</sup> and GC/IR)<sup>68</sup> which were identical with those previously reported.

*trans*- and *cis*-1,5-Heptadiene were prepared according to the literature procedure.<sup>67</sup> Bp: 92 °C (701 mmHg) (lit.<sup>67</sup> 94.0–94.5 °C (760 mmHg)). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.68 (d, 3H), 2.10 (m, 4H), 4.85–5.10 (m, 2H), 5.60–5.90 (m, 2H), 5.40 (m, 2H). The GC/MS and GC/IR spectra of *trans*-1,5-heptadiene are identical with those reported in the literature.<sup>68,69</sup> The GC/MS spectrum of *cis*-1,5-heptadiene is identical with the spectrum reported literature.<sup>69</sup> IR (gas phase):  $\nu$  3083, 3021, 2830, 1831, 1642, 1445, 993, 916, 698 cm<sup>-1</sup>.

*meso*- and *dl*-6,7-Dimethyldodecane were identified by their <sup>1</sup>H NMR, <sup>13</sup>C NMR, GC/MS, and GC/IR spectra. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.74 (d, 3H), 0.81 (d, 3H), 0.89 (t, 6H), 1.18–1.41 (m, 18H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  14.17 (C-1, *dl*- and *meso*-), 14.48, 1653 (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*-). An APT spectrum was consistent with these assignments. MS:  $m/z^+$  198 (M<sup>+</sup>). IR (vapor):  $\nu$  2960, 2933, 2876 (st, 1:2.4:1.8) cm<sup>-1</sup>; 1464, 1382 (w, 2:1) cm<sup>-1</sup>.

*cis*- and *trans*-3-Methylcyclohexyl Bromide. A mixture of the two isomers (1:4) was prepared according to the literature procedure.<sup>70</sup> <sup>1</sup>H nmr (200 MHz, DCCl<sub>3</sub>):  $\delta$  0.90 (d, 3H), 1.40–2.10 (m, 8H), 4.65 (m, 1H). Anal. Calcd for C<sub>7</sub>H<sub>13</sub>Br: C, 47.46; H, 7.34; Br, 45.20. Found: C, 47.50; H, 7.34; Br, 44.99.

*meso*- and *dl*-6,7-Dimethyl-1,11-dodecadiene were obtained by preparative glpc (100 °C, 10-ft  $\times$  1/4-in. SE-30 column) from the product mixture resulting from the addition of atomic hydrogen to 1,6-heptadiene and were identified by their <sup>1</sup>H NMR, <sup>13</sup>C NMR, GC/MS, and GC/IR spectra. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.73 (d, 3H), 0.82 (d, 3H), 1.20–1.40 (m, 10H), 2.0 (m, 4H), 4.88–5.10 (m, 4H), 5.70–5.88 (m, 2H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  14.39, 16.44 (C-13, *dl*-, *meso*-), 27.07, 27.11 (C, *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*-). MS:  $m/z^+$ , 194 (M<sup>+</sup>). IR (vapor):  $\nu$  2970, 2933, 2876 (st, 1.8:2.1:1) cm<sup>-1</sup>; 1383, 1464 (w) cm<sup>-1</sup>.

(65) Tanner, D. D.; Mahamat, H. O.; Meintzer, C. P.; Tsai, E. C.; Lu, T. T.; Yang, D. *J. Am. Chem. Soc.* **1991**, *113*, 5397.

(66) Whitesides, G. M.; Fisher, W. F., Jr.; Filippo, J. S., Jr.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871.

(67) Levy, H.; Cope, A. C. *J. Am. Chem. Soc.* **1944**, *66*, 1684.

(68) Aldrich/HP Vapor-Phase FT-IR Database.

(69) MIST/EPA/MSDS Mass Spectral Data Base, 1990, PC Version 3.0.

(70) Wiley, G. A.; Hershkovitz, R. L.; Rein, B. M.; Chung, S. C. *J. Am. Chem. Soc.* **1964**, *86*, 964.