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Reduction of Organic Halides with Tri-2-furylgermane: Stoichiometric and Catalytic Reduction

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Tri-2-furylgermane proved to be an effective reagent for the radical reduction of organic halides. Treatment of 1-bromododecane with tri-2-furylgermane in THF at 25 °C in the presence of a catalytic amount of triethylborane afforded dodecane almost quantitatively. Radical cyclization of 2-iodoethanal allyl acetal afforded five-membered products under the same reaction conditions. These reactions proceeded with $NaBH_4$ in the presence of a catalytic amount of germanium hydride. The reaction took place in water as well as in THF to give the corresponding reduced compounds in good yields.

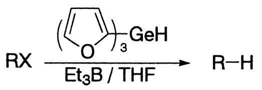
Reduction of organic halide into the corresponding hydrocarbon is one of the most important reactions in organic synthesis.[1] Among many reagents employed for this purpose, trialkyltin hydride[2] is the most reliable one and has been widely used, although its toxicity is a drawback. Very recentry, many efforts to solve this problem have been made and new compounds such as tris(trimethylsilyl)silane[3] have been developed to replace trialkyltin hydride. Here we wish to report an alternative solution. The reduction of organic halide with tri-2-furylgermane or triphenylgermane proceeds effectively in the presence of triethylborane as a radical initiator.[4] The reduction of organic halides with tri-2-furylgermane in water is also described.[5]

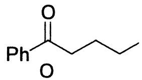
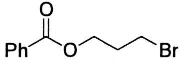
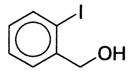
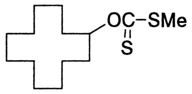
(1) Stoichiometric and Catalytic Reduction of Organic Halides in THF

The reduction of various organic halides using tri-2-furylgermane (**1**)[6] was examined. The reduction of organic halides with **1** completed smoothly in the presence of triethylborane at room temperature in THF. The representative results are shown in Table 1. Iodides and bromides were reduced effectively to give the corresponding hydrocarbons in excellent yields. In contrast, chloride such as 1-chlorododecane was recovered unchanged. Barton deoxygenation was also successful (Entry 8).

Next, the radical cyclization reaction of 2-iodoethanal allyl acetal was studied. Triethylborane (0.20 mmol) was added to a solution of *β*-iodo acetal **2a** (1.0 mmol) and tri-2-furylgermane (**1**, 1.2 mmol) in THF (10 mL) at 25 °C. The resulting mixture was stirred for 15 min. Concentration followed by silica-gel column purification afforded tetrahydrofuran derivative **3a** in 97% yield. Table 2 summarizes the results. Not only iodo acetals, generated by iodoetherization of alkenyl ethers with allylic alcohol and *N*-iodosuccinimide, but also bromo acetal **2d** and the allylic ethers of *o*-iodophenol **2e** and **2f** reacted easily with tri-2-furylgermane to give the corresponding cyclic products.

Table 1. Stoichiometric Reduction of Organic Halides with Tri-2-furylgermane



Entry	RX	Time/h	Yield/%
1	n-$C_{12}H_{25}I$	1	99
2	n-$C_{12}H_{25}Br$	2	99
3	n-$C_{10}H_{21}CH(Br)CH_3$	6	99
4	1-Bromoadamantane	2.5	83
5		2	99
6		2	99
7		1.5	93[a)]
8		1	80

a) Tri-2-furylgermane (1.5 mmol) was used.

The stoichiometric reduction of organic halides with Ph_3GeH (**4**) or n-Bu_3GeH (**5**) has been reported.[7] However, few examples of catalytic reduction with germanium hydride are known.[8] Thus, we examined the catalytic reaction. The Et_3B-induced reduction of 1-iodododecane with $NaBH_4$ (2.0 mmol) in the presence of a catalytic amount of **1** (0.10 mmol) in THF proceeded easily to give dodecane almost quantitatively. The results of the reaction with three germanium hydrides[9]: **1**, **4**, and **5**, are shown in Table 3. Several comments are worth noting. (1) Catalytic reduction was examined in several solvents such as ethanol, hexane, THF, and acetonitrile. Among them, THF gave the best result. (2) Not only primary halides (1-iodododecane and 1-bromododecane), but also secondary and tertiary halides such as 2-bromododecane and 1-bromoadamantane were reduced to the corresponding alkanes in good

Table 2. Radical Cyclization with Tri-2-furylgermane

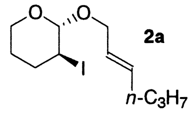
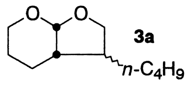
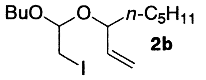
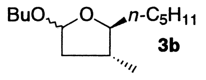
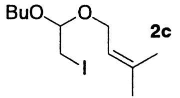
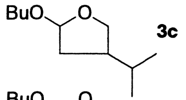
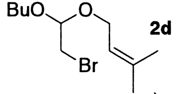
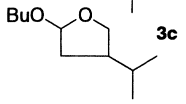
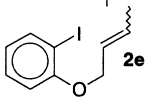
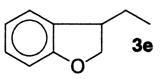
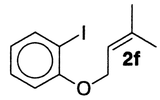
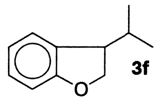
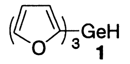
Entry	Substrate	Time/h	Product	Yield/%
1	 **2a**	0.25	 **3a**	97 (84/16)
2	 **2b**	1.5	 **3b**	63 (56/44)
3	 **2c**	0.5	 **3c**	quant (64/36)
4	 **2d**	1.5	 **3c**	81 (62/38)
5	 **2e**	2	 **3e**	89
6	 **2f**	1.5	 **3f**	88

Table 3. Germanium Hydride-Catalyzed Reduction of Organic Halides

$$\underset{(1.0\ \text{mmol})}{\text{RX}} \xrightarrow[\text{Et}_3\text{B (0.20 mmol)},\ \text{THF}]{\text{R'}_3\text{GeH (0.10 mmol)},\ \text{NaBH}_4\ \text{(2.0 mmol)}} \text{R–H}$$

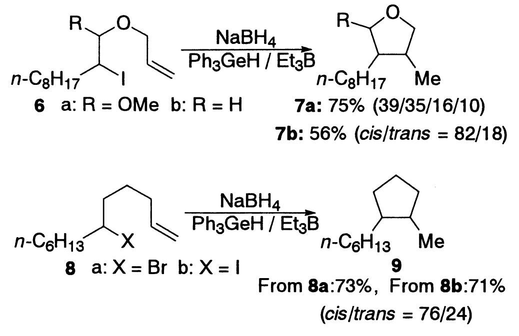
Entry	RX	R′$_3$GeH	Time/h	Yield/%
1	n-$C_{12}H_{25}I$	 **1**	4	98
2	n-$C_{12}H_{25}I$	Ph_3GeH **4**	4	98
3	n-$C_{12}H_{25}I$	n-Bu_3GeH **5**	6	89
4	n-$C_{12}H_{25}I$	**1**	4	98
5	n-$C_{12}H_{25}Br$	**4**	4	95
6	n-$C_{12}H_{25}Br$	**5**	12	89
7	n-$C_{12}H_{25}Cl$	**1**	24	5[a)]
8	n-$C_{10}H_{21}CH(Br)CH_3$	**4**	5	89
9	1-Bromoadamantane	**4**	10	73
10	$PhCOO(CH_2)_3Br$	**1**	4	90
11	$I(CH_2)_6OTHP$	**1**	1	97
12	o-I-$C_6H_4CH_2OH$	**1**	7[b)]	77

a) Starting material (95%) was recovered. b) AIBN (0.20 mmol) was used instead of Et_3B and $NaBH_4$ (4.0 mmol) was employed. The reaction was performed at reflux in THF.

yields. (3) Many functional groups such as ester and THP ether could survive under the reaction conditions. (4) Although alkyl iodide and bromide were easily reduced to the corresponding alkanes, alkyl chloride was recovered almost unchanged. (5) The amount of the catalyst could be reduced to 2 mol% without decrease of the yield of the product. For instance, treatment of 1-iodododecane (1.0 mmol) with $NaBH_4$ (2.0 mmol) at 25 °C for 12 h in the presence of **1** (0.02 mmol) provided dodecane in 96% yield.

The germanium hydride-induced radical cyclization reaction also took place in a catalytic manner. Treatment of β-iodo acetal **6a** (1.0 mmol) with Ph_3GeH (**4**, 0.10 mmol) in THF (10 mL) in the presence of $NaBH_4$ (2.0 mmol) and Et_3B (0.20 mmol) gave **7a** in 75% yield. Allyl β-iodoalkyl ether **6b**, 6-bromo-1-dodecene (**8a**), and 6-iodo-1-dodecene (**8b**) also gave the corresponding cyclization products, **7b** and **9**, in 56%, 73%, and 71% yields, respectively (Scheme 1). In these reactions, Ph_3GeH gave better yields than tri-2-furylgermane (**1**). For instance, the use of **1** in the reaction of **6b** provided **7b** in only 20% yield.

(2) Reduction of Organic Halides with Tri-2-furylgermane in Water

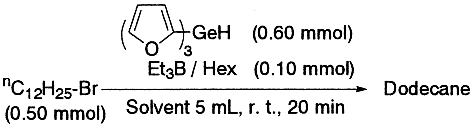


Scheme 1.

Recently, there has been increasing recognition that organic reactions carried out in aqueous media or in water may offer advantages over those occurring in organic solvents. For instance, it was reported that the Diels–Alder reaction was accelerated by using water as a solvent.[10,11] We also reported the facile atom-transfer cyclization of allyl iodoacetate mediated by triethylborane in water.[12] Here we describe the results of the reduction of organic halides with tri-2-furylgermane in water.

First, the reduction of 1-bromododecane with tri-2-furylgermane in various solvents was examined. Treatment of 1-bromododecane (1.0 mmol) with tri-2-furylgermane (1.2 mmol) in the presence of triethylborane (1.0 M hexane solution, 0.20 mL, 0.20 mmol) at 25 °C for 20 min gave dodecane in 90% (THF), 74% (benzene), 44% (hexane), and 87% (water) yields, respectively. Without a solvent, dodecane was obtained in 81% yield (Table 4).

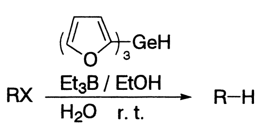
Table 4. Reduction of 1-Bromododecane in Various Solvents



Entry	Solvent	Yield/%	$^{n}C_{12}H_{25}$–Br/%
1	THF	90	5
2	benzene	74	19
3	hexane	44	51
4[a)]	H_2O	87	6
5	neat	81	9

a) A methanol solution of Et_3B (1.0 M, 0.10 mL, 0.10 mmol) was used.

Table 5. Reduction of Organic Halides with Tri-2-furylgermane in Water Using Triethylborane as an Initiator



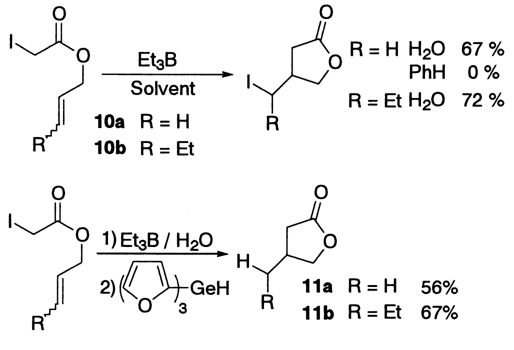
Entry	RX	Time/min	Yield/%
1	n-$C_{12}H_{25}I$	5	85
2	n-$C_{12}H_{25}Br$	25	89
3	n-$C_{10}H_{21}CH(Br)CH_3$	15	83
4	1-Bromoadamantane	20	92

We, then studied the triethylborane-induced radical reduction of several organic halides with tri-2-furylgermane in water. Four examples are shown in Table 5. The secondary and tertiary alkyl halides as well as primary ones were easily reduced to the corresponding hydrocarbons in excellent yields. Ph_3GeH is also effective for the reduction of organic halides in water. For example, treatment of 1-bromododecane with Ph_3GeH in water afforded dodecane in 80% yield along with the starting material (8%). Thus, tri-2-furylgermane is more effective than Ph_3GeH.

Next, the reduction using V-70 [2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile)][13] as a radical initiator instead of triethylborane was examined in order to eliminate the effect of alcohol such as methanol or ethanol which was used to obtain a solution of triethylborane.[14] V-70 was added to a suspension of organic halide and tri-2-furylgermane in water and the whole mixture was stirred at 80 °C for 20 min ~ 4.5 h. The representative results are shown in Table 6. All organic halides examined were converted into the corresponding reduction products in good to excellent yields, irrespective of the solubility to water. The functional groups such as ester and THP ether survived under the reaction conditions.

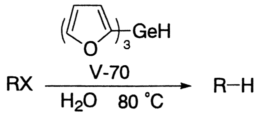
Finally, the one-pot conversion of allylic iodoacetates into γ-lactones was examined. Triethylborane was added to a suspension of allyl iodoacetate **10a** in water and the mixture was stirred at 25 °C for 1.5 h to give β-iodomethyl-γ-butyrolactone. Then, tri-2-furylgermane was subsequently added to the resulting solution of the β-iodomethyl-γ-butyrolactone and the whole was stirred for another 5 h to give γ-lactone **11a** in 56% overall yield (Scheme 2). In a similar fashion, β-propyl-γ-butyrolactone was obtained in 67% yield starting from **10b**.

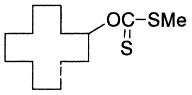
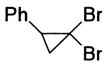
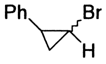
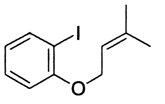
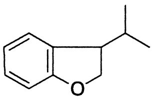
In conclusion, (1) Triethylborane-induced radical reduction of organic halides with tri-2-furylgermane in THF proceeded very easily to give the corresponding reduced compounds in good to excellent yields. (2) Radical cyclization of 2-haloethanal allyl acetal afforded five-membered products under the same reaction conditions. (3) The reduction completed with $NaBH_4$ in the presence of a catalytic amount of germanium hydride (tri-2-furylgermane, Ph_3GeH, or n-Bu_3GeH). (4) Water could be used as a solution in place of THF. The acceleration of the reaction could not be observed by using water as a solvent in this radical reduction of organic halides. Treatment of 1-bromododecane with tri-2-furylgermane without a solvent provided dodecane in 81% yield, which is similar to the results



Scheme 2.

Table 6. V-70 Mediated Reduction of Organic Halides with Tri-2-furylgermane in Water



Entry	RX	Time/h	Yield/%
1	*n*-$C_{12}H_{25}I$	0.5	80
2	*n*-$C_{12}H_{25}Br$	0.5	83
3	*n*-$C_{10}H_{21}CH(Br)CH_3$	0.33	82
4	1-Bromoadamantane	1	92
5	$PhCOO(CH_2)_3Br$	1	99
6	$I(CH_2)_6OTHP$	0.25	88
7		0.5	63
8	$HO(CH_2CH_2O)_3CH_2CH_2I$	1	97
9		3.5	 68 (*cis*/*trans* = 70/30)
10		4.5	 75

in THF and in water. The reaction rates were almost the same in water, in THF, and without a solvent. Thus, in a small scale reaction, a solvent-free reaction is recommended. In contrast, the use of water as a solvent would be favorable in order to suppress the heat of an exothermic reaction. (5) Direct conversion of allyl iodoacetate into γ-butyrolactone could be performed by sequential treatment with triethylborane and tri-2-furylgermane in water.

Experimental

The NMR spectra (^1H and ^{13}C) were recorded on a Varian GEMINI 300 spectrometer in $CDCl_3$; tetramethylsilane (TMS) was used as an internal standard. The IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Synthesis of Tri-2-furylgermane. Butyllithium (250 mL, 1.6 M hexane solution, 400 mmol) was added to a solution of furan (30.0 g, 400 mmol) in THF (250 mL) at 0 °C. The solution immediately turned yellow and the resulting mixture was stirred for 30 min at 0 °C. Then a solution of germanium tetrachloride (11 mL, 90 mmol) in benzene (80 mL) was added at 0 °C and the solution was stirred for another 3 h at 25 °C. The mixture was poured into water and extracted with ethyl acetate (50 mL×3). The combined organic layer was dried and concentrated in vacuo to give a solid. Recrystallization from toluene provided tetra-2-furylgermane (26 g, 77 mmol) in 85% yield. Lithium metal (0.830 g, 120 mmol) was added to a solution of tetra-2-furylgermane (10 g, 30 mmol) in THF (30 mL) and the resulting mixture was stirred for 1.5 h at 25 °C. Extractive workup (EtOAc, brine) followed by silica-gel column purification gave tri-2-furylgermane (**1**, 5.8 g, 21 mmol) in 70% yield. **1**: IR (neat) 2086, 1551, 1454, 1362, 1206, 1151, 1103, 1062, 1004, 898, 884, 819, 741, 594 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.78 (s, 1H), 6.47 (dd, J = 3.3, 1.5 Hz, 3H), 6.81 (d, J = 3.3 Hz, 3H), 7.73 (d, J = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 110.01, 121.86, 147.74, 150.59. Found: C, 52.18; H, 3.78%. Calcd for $C_{12}H_{10}GeO_3$: C, 52.45; H, 3.67%.

General Procedure for the Stoichiometric Reduction of Organic Halides in THF. Reduction of 1-bromododecane is representative. A hexane solution of Et_3B (1.0 M, 0.10 mL, 0.10 mmol) was added to a solution of 1-bromododecane (0.25 g, 1.0 mmol) and tri-2-furylgermane (0.33 g, 1.2 mmol) in THF (10 mL) at room temperature under an argon atmosphere. After stirring for 2 h at room temperature, the reaction mixture was concentrated in vacuo. The residual oil was subjected to silica-gel column chromatography to give dodecane in 99% yield.

The Catalytic Reduction of Organic Halides in THF. A typical procedure is as follows. Et_3B (1.0 M hexane solution, 0.10 mL, 0.10 mmol) and $NaBH_4$ (0.076 g, 2.0 mmol) were added to a solution of 1-bromododecane (0.25 g, 1.0 mmol) and tri-2-furylgermane (0.027 g, 0.10 mmol) in THF (10 mL) at room temperature under an argon atmosphere. After stirring for 4 h at room temperature, the reaction mixture was poured into aqueous HCl (1 M) and extracted with hexane three times. Combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was subjected to silica-gel column chromatography to give dodecane in 98% yield.

The Reduction of Organic Halides in the Presence of V-70 in Water. V-70 (0.015 g, 0.050 mmol) was added to a suspension of 1-bromododecane (0.12 g, 0.50 mmol) and tri-2-furylgermane (0.16 g, 0.60 mmol) in water (5 mL) at room temperature under an argon atmosphere. The mixture was heated at 80 °C for 30 min. The reaction mixture was extracted with hexane three times. Evaporation of the solvent and purification gave dodecane in 83% yield.

Cyclization of Allyl Iodoacetate in Water. Et_3B (1.0 M methanol solution, 0.1 mL, 0.1 mmol) was added to a suspension of allyl iodoacetate (0.22 g, 1.0 mmol) in water (50 mL) at room temperature under an argon atmosphere and the mixture was stirred for 1.5 h. Tri-2-furylgermane (0.33 g, 1.2 mmol) was added and the whole was stirred for another 5 h. The reaction mixture was extracted with ethyl acetate three times and the organic layer was concentrated. Silica-gel column purification of the crude product provided β-methyl-γ-butyrolactone **11a** in 56% yield.

Characterization Data. Spectral data for the compounds **2b**–**f**, **3b**–**f**, **7**, **10**, and **11** are found in the literature.[12,15]

3-Iodo-2-(2-hexenyloxy)tetrahydropyran (2a). IR (neat) 2912, 2846, 1672, 1463, 1436, 1354, 1303, 1202, 1122, 1068, 866, 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.89 (t, J = 7.2 Hz, 3H), 1.42 (tq, J = 7.2, 7.2 Hz, 2H), 1.50–1.61 (m, 1H), 1.69–1.80 (m, 1H), 1.94–2.04 (m, 1H), 2.02 (dt, J = 6.6, 7.2 Hz, 2H), 2.31–2.41 (m, 1H), 3.56 (ddd, J = 11.7, 7.8, 3.9 Hz, 1H), 3.93–4.00 (m, 2H), 4.09 (ddd, J = 8.1, 4.5, 4.5 Hz, 1H), 4.18 (dd, J = 11.7, 6.6 Hz, 1H), 4.66 (d, J = 4.5 Hz, 1H), 5.56 (ddd, J = 15.3, 6.6, 6.6 Hz, 1H), 5.71 (ddd, J = 15.3, 6.6, 6.6 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 13.55, 22.03, 25.40, 29.39, 32.61, 34.24, 63.35, 68.85, 101.27, 125.56, 135.38. Found: C, 42.45; H, 6.04%. Calcd for $C_{11}H_{19}IO_2$: C, 42.60; H, 6.17%.

7-Butyl-2,9-dioxabicyclo[4.3.0]nonane (3a, Mixture of Diastereomers, 84/16). IR (neat) 2924, 2856, 1724, 1467, 1403, 1253, 1146, 1090, 1023, 949, 902, 870 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, J = 6.9 Hz, 3H), 1.10–1.45 (m, 7H), 1.54–1.98 (m, 4H), 2.25–2.37 (m, 1H), 3.42 (ddd, J = 11.4, 11.4, 1.8 Hz, 0.16H), 3.54 (dd, J = 8.4, 8.4 Hz, 0.16H), 3.60–3.69 (m, 0.84×2H), 3.70–3.80 (m, 0.84H), 3.80–3.94 (m, 0.16H), 3.95 (dd, J = 8.1, 8.1 Hz, 0.84H), 4.28 (dd, J = 8.4, 8.4 Hz, 0.16H), 5.00 (d, J = 3.6 Hz, 0.16H), 5.28 (d, J = 3.6 Hz, 0.84H); ^{13}C NMR (CDCl$_3$): For major isomer, δ 13.83, 19.05, 22.74, 23.12, 26.55, 30.35, 36.41, 40.91, 60.89, 70.12, 102.06. For minor isomer: δ 13.83, 20.61, 22.30, 22.78, 30.62, 32.32, 37.74, 44.06, 64.42, 74.26, 102.06. Found: C, 71.57; H, 11.21%. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94%.

2-Iodo-1-methoxy-1-(2-propenyloxy)decane (6a, Mixture of Diastereomers, 80/20). IR (neat) 2922, 2850, 1459, 1102, 1048, 925 cm^{-1}; ^{1}H NMR (CDCl$_3$): For major isomer, δ 0.86 (t, J = 6.6 Hz, 3H), 1.12–1.42 (m, 11H), 1.42–1.66 (m, 1H), 1.76 (dt, J = 7.2, 6.9 Hz, 2H), 3.39 (s, 3H), 4.03–4.13 (m, 1H), 4.06 (dt, J = 6.9, 7.2 Hz, 1H), 4.18 (dd, J = 5.4, 12.9 Hz, 1H), 4.36 (d, J = 5.4 Hz, 1H), 5.19 (d, J = 10.5 Hz, 1H), 5.27 (d, J = 17.1 Hz, 1H), 5.92 (ddt, J = 10.5, 17.1, 5.4 Hz, 1H); ^{13}C NMR (CDCl$_3$): For major isomer, δ 13.95, 22.51, 28.69, 29.10, 29.25, 29.31, 31.71, 33.82, 36.54, 54.69, 68.76, 105.18, 117.45, 134.09. Found: C, 47.37; H, 7.76%. Calcd for $C_{14}H_{27}IO_2$: C, 47.46; H, 7.68%.

2-Iodo-1-(2-propenyloxy)decane (6b). IR (neat) 2922, 2852, 1460, 1381, 1349, 1073, 993, 925 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.86 (t, J = 6.6 Hz, 3H), 1.18–1.42 (m, 11H), 1.44–1.59 (m, 1H), 1.67–1.87 (m, 2H), 3.60 (dd, J = 10.2, 7.4 Hz, 1H), 3.70 (dd, J = 10.2, 6.0 Hz, 1H), 4.01 (d, J = 5.4 Hz, 2H), 4.10–4.19 (m, 1H), 5.18 (dd, J = 10.5, 1.7 Hz, 1H), 5.27 (dd, J = 17.1, 1.7 Hz, 1H), 5.89 (dddd, J = 17.1, 10.5, 7.4, 6.0 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 13.98, 22.54, 28.74, 29.13, 29.22, 29.29, 31.74, 34.28, 36.43, 71.85, 75.79, 117.44, 134.52. Found: C, 48.36; H, 7.49%. Calcd for $C_{13}H_{25}IO$: C, 48.16; H, 7.77%.

6-Iodo-1-dodecene (8b). IR (neat) 2924, 2854, 1642, 1378, 1213, 992, 912, 723 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.88 (t, J = 6.9 Hz, 3H), 1.20–1.78 (m, 12H), 1.78–1.94 (m, 2H), 1.98–2.16 (m, 2H), 4.12 (tt, J = 4.5, 8.4 Hz, 1H), 4.97 (d, J = 10.5 Hz, 1H), 5.01 (d, J = 17.1 Hz, 1H), 5.80 (ddt, J = 10.5, 17.1, 6.6 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 13.93, 22.48, 28.40, 28.63, 29.37, 31.57, 32.80, 39.89, 40.08, 40.60, 114.96, 138.37. Found: C, 49.24; H, 8.01%. Calcd for $C_{12}H_{23}I$: C, 48.99; H, 7.88%.

1-Hexyl-2-methylcyclopentane (9, Mixture of Diastereomers, 76/24). IR (neat) 2920, 2854, 1458, 1377, 722 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.77 (d, J = 6.9 Hz, 0.76×3H), 0.88 (t, J = 6.9Hz, 3H), 0.95 (d, J = 6.3 Hz, 0.24×3H), 1.00–1.88 (m, $0.76 \times 17\text{H} + 0.24 \times 18\text{H}$), 1.90–2.05 (m, 0.76H); ^{13}C NMR (CDCl$_3$): For major isomer, δ 14.01, 14.67, 22.41, 22.63, 28.73, 29.67, 29.71, 30.46, 31.90, 33.49, 35.90, 43.33. Found: C, 85.68; H, 14.58. Calcd for $C_{12}H_{24}$: C, 85.63; H, 14.37%.

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