Dihaloadamantanes: Ring Closure versus Rearrangement or Halogen-Displacement Reactions

Kata Mlinarić-Majerski,*[a] Jelena Veljković,[a] Mira Kaselj,[a] and Alan P. Marchand[b]

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Three dihaloadamantanes [i.e., 2-bromo-1-(chloromethyl)adamantane (**1**), 1-(bromomethyl)-2-chloroadamantane (**2**) and 2-bromo-1-(bromomethyl)adamantane (**3**)] were synthesized, and their corresponding ring-closing reactions, performed by using Na metal or alkyllithium reagents, were studied. Compound **1** reacted with Na in toluene or in tetraglyme to afford 1,2-methanoadamantane (**4**) as the major product. However, the corresponding reactions, when performed by using **2** and **3** as substrates, produced methyladamantane (**5**) or 4-methyleneprotoadamantane (**6**) as the major reaction products. The corresponding reactions of **1** and **2** with *t*BuLi or *n*BuLi afforded small quantities of **4**, **5** and **6** along with the corresponding monohalides, that is, 1-(chloromethyl)adamantane (**7**) and 2-chloro-1-methyladamantane (**8**), which constituted the major products of these reactions.

Introduction

A conceptually simple route to cycloalkanes involves intramolecular Wurtz-type coupling of dihaloalkanes with organolithium reagents or with metals such as Li, K, and Na. Despite mechanistic controversy,[1] organolithium-promoted cyclization reactions provide a useful tool that has been applied extensively to the synthesis of cyclic compounds. Intramolecular ring closure of α,γ-dihalides with alkyllithium reagents has been used to prepare small-ring compounds, including cyclopropanes[2] and [1.1.1]propellane[3] and some of its derivatives.[4] The same approach has been used to prepare tricyclo[2.1.0.0^{1,3}]pentane[5] and bridged [3.3.3]fenestrane.[6] Sodium- and potassium-promoted reductive cyclizations have been used, for example, to synthesize [2.2.1]propellane,[7] [3.1.1]propellane,[8] [3.2.1]propellane,[9] adamantane-annulated [3.3.1]propellane,[10] bicyclobutane,[11] and 1,2-methanoadamantane.[12]

In our studies of the ring-closure reactions of α,γ-dihaloadamantanes, we have observed that 1,2-methanoadamantane (**4**) is the major product formed by the reaction of 2-bromo-1-(chloromethyl)adamantane (**1**) with Na.[12] In an effort to obtain a better yield of this extremely strained molecule,[12] we have studied the ring-closure reactions of three alkyl halides, that is, 2-bromo-1-(chloromethyl)adamantane (**1**), 1-(bromomethyl)-2-chloro-adamantane (**2**) and 2-bromo-1-(bromomethyl)adamantane (**3**), with Na and with alkyllithium reagents.

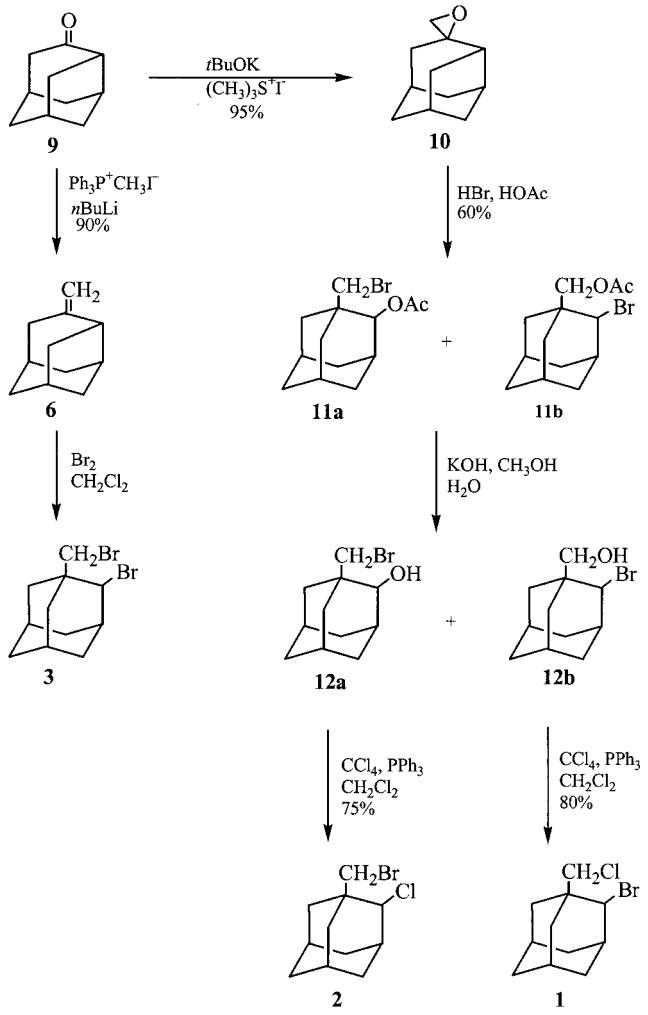
[a] Ruder Bosković Institute, Department of Chemistry and Biochemistry,
P. O. Box 180, 10000 Zagreb, Croatia
Fax: (internat.) + 385-1-4680-196
E-mail: majerski@irb.hr
[b] Department of Chemistry, University of North Texas, Denton, Texas 76203-5070, USA
E-mail: marchand@unt.edu

Results and Discussion

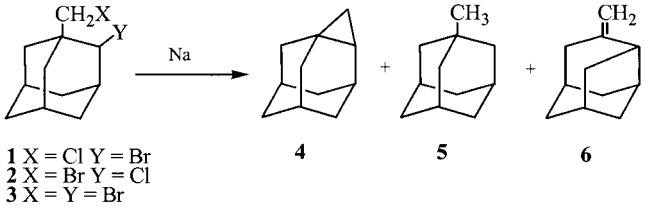
2-Bromo-1-(chloromethyl)adamantane (**1**), 1-(bromomethyl)-2-chloroadamantane (**2**), and 2-bromo-1-(bromomethyl)adamantane (**3**) were synthesized from protoadamantan-4-one (**9**)[13] by using the procedures outlined in Scheme 1. Thus, reaction of **9** with $Me_2S{=}CH_2$ afforded a mixture of 4-*exo*- and 4-*endo*-(epoxymethylene)protoadamantane (**10**; product ratio *exo*-**10**/*endo*-**10** = 3:2).[14] Subsequent reaction of the mixture of **10** thereby obtained with 33% HBr/HOAc resulted in the formation of a mixture of **11a** and **11b**. Alkaline hydrolysis of this mixture of **11a** and **11b** afforded a mixture of the corresponding alcohols, that is, **12a** and **12b**, respectively.

Compounds **12a** and **12b** were separated by column chromatography on silica gel by using a 0−100% CH_2Cl_2/pentane gradient elution scheme. Subsequent reaction of **12a** and **12b** with the Ph_3P/CCl_4 reagent afforded **2** (75% yield) and **1** (80%), respectively. Dibromide **3** was prepared in 60% overall yield by Wittig reaction of **9** with $Ph_3P{=}CH_2$ followed by addition of Br_2 across the C=C double bond in the resulting alkene **6**.

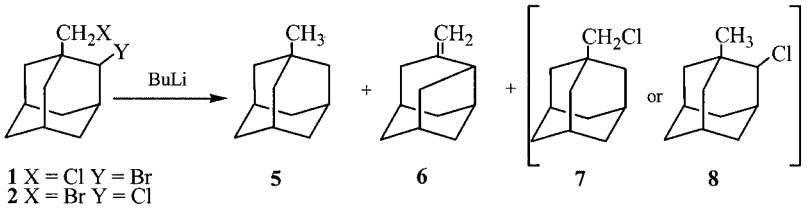
Compounds **1**, **2** and **3** were treated with Na/$PhCH_3$ at 105 °C, and the mixture of products obtained from each reaction was subjected to GLC analysis; the results thereby obtained are presented in Scheme 2 and Table 1. 1,2-Methanoadamantane (**4**), the product formed by reductive



Scheme 1



Scheme 2



Scheme 3

Table 1. Reactions of **1**, **2** and **3** with metallic sodium

Solvent	Compound	Products[a] (%)			Yield (%)[b]
		4	**5**	**6**	
Toluene	**1**	52	45	3	72
	2	–	21	75	70
	3	6	25	69	41
Tetraglyme	**1**	49	45	6	70
	2	–	98	2	80
	3	19	77	4	43

[a] Product composition was determined by GLC by using a capillary column DB-210 maintained at 90 °C for 3 min and then temperature-programmed from 90 to 180 °C at a rate of 10 °C/min. [b] Yield of isolated products.

cyclization, was observed to be the major product only in the case of reaction of **1** with Na in toluene. Under the same reaction conditions, dihalides **2** and **3** reacted with Na to afford primarily 4-methyleneprotoadamantane (**6**).[15]

Interestingly, when tetraglyme was used as the solvent in the reaction of **2** and **3** with Na, 1-methyladamantane (**5**) was obtained as the major reaction product. It seems likely that a charged (rather than radical) intermediate is involved when reactions of **2** and **3** with Na are performed in the more highly polar solvent (i.e., tetraglyme). However, it should be noted that the relative yields of products **4**, **5** and **6** remained relatively constant when the reaction of **1** with Na was carried out in either toluene or tetraglyme as solvent.

As noted previously, a cyclopropane ring can be prepared readily by treating α,γ-dihalides with an alkyllithium reagent. Thus, we attempted to prepare 1,2-methanoadamantane (**4**) by treating **1** and **2** with RLi. Formally, this reaction can be viewed as an intramolecular Wurtz-type coupling of an intermediate 1-lithio-3-haloalkane that results by an initial metal/halogen interchange. It is generally accepted that the mechanism of the Wurtz reaction[1] involves two stages, namely, reduction and alkyl coupling, which might proceed by S_N1 or S_N2 reaction mechanisms or, alternatively, might involve free radical intermediates. Reactions of alkyllithium reagents with alkyl halides are believed to involve free alkyl radicals.[16] The initial mechanistic step is thought to proceed by electron transfer from an alkyllithium "carbanion" to the alkyl halide with concomitant formation of diradicals.[17] For alkylsodium, however, the results of some studies have been rationalized in terms of S_N2 alkyl coupling, while other investigators have interpreted their results in terms of a free-radical mechanism.[18]

The results obtained for reactions of **1** and **2** with *n*BuLi and *t*BuLi, respectively, are summarized in Scheme 3 and Table 2. When these reactions were performed in pentane/Et_2O solution, a mixture of products was obtained in which 1-(chloromethyl)adamantane (**7**)[19] and 2-chloro-1-methyladamantane (**8**)[20] predominated.

Table 2. Reaction of **1** and **2** with alkyllithium reagent (RLi)

Compound	Base	Products [a] (%)					Yield (%)[b]
		4	**5**	**6**	**7**	**8**	
1	*t*BuLi	trace	3	4	92	–	85
	*n*BuLi[c]	4	3	7	33	–	80
2	*t*BuLi	–	3	3	–	94	88
	*n*BuLi[c]	–	5	6	–	33	82

[a]Product composition was determined by GLC-MS by using a capillary column DB-210 maintained at 90 °C for 30 min and then temperature-programmed from 90 to 180 °C at a rate of 10 °C/min. [b] Yield of isolated products. [c] In addition, **1** (53%) and **2** (56%) were present among the isolated products.

The product that might have been formed by reductive cyclization (i.e., **4**) was not present among the mixture of products obtained by the reaction of **2** with RLi. Similarly, the corresponding reaction of **1** with RLi afforded only traces of **4**.

Conclusion

Procedures for the preparation of 2-bromo-1-(chloromethyl)adamantane (**1**), 1-(bromomethyl)-2-chloroadamantane (**2**) and 2-bromo-1-(bromomethyl)adamantane (**3**) are described along with the experimental results obtained by treating each of these dihaloadamantanes with Na metal or with alkyllithium reagents. The experimental results clearly indicate that the reactions of **1** and **2** with Na and RLi reagents lead to the formation of different products, thereby suggesting that reactions of **1** and **2** with Na and with RLi proceed by different mechanistic pathways.

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were obtained by using JEOL FX90Q and Varian Gemini 300 nuclear magnetic resonance spectrometers. IR spectra were recorded with a Perkin–Elmer M-297 spectrophotometer. High-resolution electron impact (EI) mass spectra were obtained by using an EXTREL FTMS 2001 mass spectrometer. The purity of all compounds was determined by GLC and/or by ^{13}C NMR spectra analyses. GLC analyses were carried out with a Varian 3300 gas chromatograph equipped with a DB-210 capillary column. GLC-MS analyses were performed by using a Varian-Saturn II spectrometer. Melting points were determined with a Kofler apparatus and are uncorrected. Unless stated otherwise, reagent grade solvents were employed. Starting materials 4-protoadamantanone[13] and 4-(epoxymethylene)protoadamantane[14] were synthesized according to published procedures.

1-(Bromomethyl)-2-adamantyl Acetate (11a) and 2-(Bromoadamant-1-yl)methyl Acetate (11b): A mixture of oxiranes **10**[14] (1.0 g, 6.1 mmol), glacial HOAc (10 mL) and 30% HBr/HOAc (18 mL) was stirred at ambient temperature for 3 h, at which time the reaction was quenched by pouring it onto ice (50 g). The resulting mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. A mixture of **11a** and **11b** (1.0 g, 60%; product ratio **11a/11b**, 2:1) was thereby obtained as a pale yellow, viscous oil. This material obtained was used in the next reaction, without further purification. Subsequently, the mixture of **11a** and **11b** was saponified, and the resulting mixture of alcohols (i.e., **12a** and **12b**) was subjected to column chromatographic purification. In this way, isomerically pure **12a** and **12b** were obtained, and each compound was fully characterized (vide infra). Finally, isomerically pure samples of **12a** and **12b** were re-esterified by using Ac_2O/pyridine and thereby were converted into isomerically pure **11a** and **11b**. Compound **11a** was obtained as a colorless, viscous oil. IR (KBr, film): $\tilde{\nu}$ = 2920 (s), 2850 (m), 1740 (s), 1450 (m), 1360 (m), 1240 (s), 1030 cm^{-1} (m). ^{1}H NMR ($CDCl_3$): δ = 1.40–2.18 (m, 16 H, including a CH_3 singlet that appears at δ = 2.08 ppm), 3.07 (*A*B, J_{AB} = 10.0 Hz, 1 H), 3.34 (A*B*, J_{AB} = 10.0 Hz, 1 H), 4.89 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.7 (q), 27.2 (d, 2 C), 30.5 (t), 31.4 (d), 35.4 (t), 35.5 (t), 36.1 (t), 36.0 (s), 39.4 (t), 42.5 (t), 76.2 (d), 169.6 (s) ppm. Exact mass (EI-HRMS): $C_{13}H_{19}BrO_2$: calcd. 286.056292, found 286.053637. Compound **11b** was obtained as a colorless, viscous oil. IR (KBr, film): $\tilde{\nu}$ = 2900 (s), 2840 (m), 1740 (s), 1450 (m), 1230 (s), 1030 (m), 730 cm^{-1} (m). ^{1}H NMR ($CDCl_3$): δ = 1.30–2.36 (m, 16 H, including a CH_3 singlet that appears at δ = 2.08 ppm), 3.76 (*A*B, J_{AB} = 11.0 Hz, 1 H), 3.91 (A*B*, J_{AB} = 11.0 Hz, 1 H), 4.58 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.7 (q), 27.1 (d), 27.6 (d), 31.3 (t), 33.0 (t), 36.8 (d), 37.1 (t), 37.5 (s), 38.0 (t), 40.0 (t), 64.6 (d), 71.9 (t), 170.8 (s) ppm. Exact mass (EI-HRMS): $C_{13}H_{19}BrO_2$: calcd. 286.056292, found 286.054373.

1-(Bromomethyl)-2-hydroxyadamantane (12a) and 2-Bromo-1-(hydroxymethyl)adamantane (12b): A solution of **11a** and **11b** (1.0 g, 3.5 mmol), KOH (1.00 g, 17.8 mmol) in 50% aqueous MeOH (58 mL) was stirred at ambient temperature for 48 h. Water (50 mL) was added to the reaction mixture, and the resulting mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. A mixture of **12a** and **12b** (680 mg, 80%) was thereby obtained as a colorless oil. This mixture of esters was separated by column chromatography on alumina (activity grade II/III) by using a CH_2Cl_2/pentane gradient elution scheme. Workup of the chromatography fraction that was collected by eluting the column with 60% CH_2Cl_2/pentane afforded isomerically pure **12a** (405 mg, 47%) as a colorless microcrystalline solid. M.p. 56–57 °C. IR (KBr): $\tilde{\nu}$ = 3430 (s), 2900 (s), 2850 (m), 1450 (m), 1040 cm^{-1} (m). ^{1}H NMR ($CDCl_3$): δ = 1.25–2.20 (m, 14 H), 3.13 (*A*B, J_{AB} = 10.0 Hz, 1 H), 3.55 (A*B*, J_{AB} = 10.0 Hz, 1 H), 3.81 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.6 (d, 2 C), 30.2 (t), 34.8 (d), 35.0 (t), 36.2 (t), 36.6 (t), 37.5 (s), 39.5 (t), 44.2 (t), 73.7 (d) ppm. Exact mass (EI-HRMS): $C_{11}H_{17}BrO$: calcd. 244.045727, found 244.045526. Continued elution of the chromatography column with CH_2Cl_2 afforded a second fraction, which afforded isomerically pure **12b** (210 mg, 25%) as a colorless microcrystalline solid. M.p. 137–138 °C (ref.[14a] m.p. 138 °C; ref.[14c] m.p. 136–137 °C). IR (KBr): $\tilde{\nu}$ = 3250 (s), 2900 (s), 2840 (m), 1450 (m), 1030 (s), 730 cm^{-1} (s). ^{1}H NMR ($CDCl_3$): δ = 1.15–2.40 (m, 14 H) 3.18 (*A*B, J_{AB} = 11.0 Hz, 1 H), 3.52 (A*B*, J_{AB} = 11.0 Hz, 1 H), 4.64 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.2 (d), 27.7 (d), 31.6

(t), 32.9 (t), 37.0 (d), 37.3 (t), 38.1 (t), 39.0 (s), 40.0 (t), 66.0 (d), 71.2 (t) ppm.

1-(Bromomethyl)-2-chloroadamantane (2): A solution of Ph_3P (560 mg 2.1 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of **12a** (400 mg, 1.63 mmol) in CCl_4 (5 mL). The resulting mixture was stirred at 76 °C for 24 h, at which time the reaction mixture was cooled to ambient temperature and was then concentrated in vacuo. The residue was purified by column chromatography on alumina (activity grade II/III) by eluting with pentane. Pure **2** (370 mg, 75%) was thereby obtained as a colorless microcrystalline solid. M.p. 54−55 °C. IR (KBr): $\tilde{\nu}$ = 2910 (s), 2840 (m), 1450 (m), 1275 (m), 800 (m), 760 cm^{-1} (m). ^1H NMR ($CDCl_3$): δ = 1.30−2.30 (m, 13 H), 3.10 (*A*B, J_{AB} = 10.1 Hz, 1 H), 3.53 (A*B*, J_{AB} = 10.1 Hz, 1 H), 4.34 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.5 (d), 27.7 (d), 30.4 (t), 34.9 (t), 36.1 (d), 36.7 (t), 37.4 (t), 38.0 (s), 40.7 (t), 44.4 (t), 68.7 (d) ppm. Exact mass (EI-HRMS): $C_{11}H_{16}BrCl$: calcd. 262.011840, found 262.014106.

2-Bromo-1-(chloromethyl)adamantane (1): A solution of Ph_3P (280 mg 1.05 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of **12b** (200 mg, 0.82 mmol) in CCl_4 (4 mL). The resulting mixture was stirred at 76 °C for 24 h, at which time the reaction mixture was cooled to ambient temperature and was then concentrated in vacuo. The residue was purified by column chromatography on alumina (activity grade II/III) by eluting with pentane. Pure **1** (170 mg, 80%) was thereby obtained as a colorless microcrystalline solid. M.p. 69−70 °C. IR (KBr): $\tilde{\nu}$ = 2920 (s), 2850 (m), 1450 (m), 1290 (m), 750 (s), 710 cm^{-1} (m). ^1H NMR ($CDCl_3$): δ = 1.25−2.35 (m, 13 H), 3.20 (AB, J_{AB} = 10.7 Hz, 1 H), 3.57 (A*B*, J_{AB} = 10.7 Hz, 1 H), 4.61 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.4 (d), 27.7 (d), 31.3 (t), 34.9 (t), 36.8 (d), 37.0 (t), 37.8 (t), 38.5 (s), 39.8 (t), 55.0 (t), 64.8 (d) ppm. Exact mass (EI-HRMS): $C_{11}H_{16}BrCl$: calcd. 262.011840, found 262.014709.

4-(Methylene)protoadamantane (6):[21,22] Compound **6** was prepared in 90% yield by applying a standard Wittig reaction procedure.[23] Thus, a solution of *n*BuLi in hexane (1.6 m solution, 6.7 mL, 10.7 mmol) was added dropwise with stirring to a suspension of $CH_3Ph_3P^+I^-$ (4.30 g, 10.7 mmol) in dry Et_2O (20 mL) under N_2 at ambient temperature. The color of the reaction mixture gradually changed to orange. Once all of the organolithium reagent had been added, the reaction mixture was refluxed under N_2 with stirring for 0.5 h. A solution of **9** (930 mg, 6.2 mmol) in dry Et_2O (5 mL) was then added dropwise with stirring to the reaction mixture. After the addition of **9** had been completed, the resulting mixture was refluxed with stirring for 2 h, during which time the reaction mixture became colorless, and $Ph_3P{=}O$ was separated from the reaction mixture as a colorless precipitate. The precipitate was removed by suction filtration, and the residue was washed with Et_2O (2 × 10 mL). The ethereal filtrate was washed with water (3 × 10 mL), dried ($MgSO_4$), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on alumina (activity grade II/III) by eluting with pentane. Pure **6** (734 mg, 80%) was thereby obtained as a colorless, waxy solid. M.p. 20−24 °C [ref.[21c] b.p. 209 °C]. IR (KBr, film): $\tilde{\nu}$ = 3070 (w), 2920 (s), 2860 (m), 1650 (w), 1450 (w), 880 cm^{-1} (m). ^1H NMR ($CDCl_3$): δ = 1.35−2.90 (m, 14 H), 4.59 (s, 1 H), 4.73 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.1 (d), 33.7 (t), 35.9 (d), 36.9 (d), 37.8 (t), 38.5 (t), 39.3 (t), 41.2 (t), 44.6 (d) 106.1 (t), 151.5 (s) ppm.

2-Bromo-1-(bromomethyl)adamantane (3): A solution of Br_2 (470 mg, 2.8 mmol) in CH_2Cl_2 (4 mL) was added dropwise with stirring to a solution of **6** (400 mg, 2.7 mmol) in CH_2Cl_2 (7 mL) at ambient temperature. After all of the Br_2/CH_2Cl_2 solution had been added, the reaction mixture was stirred at ambient temperature for 15 min, during which time the solution became colorless. The reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography on alumina (activity grade II/III) by eluting with pentane. Pure **3** (620 mg, 75%) was thereby obtained as a colorless microcrystalline solid. M.p. 63−65 °C. IR (KBr): $\tilde{\nu}$ = 2910 (s), 2840 (m), 1450 (m), 1270 (m), 730 (s) 650 cm^{-1} (m). ^1H NMR ($CDCl_3$): δ = 1.30−2.40 (m, 13 H), 3.12 (*A*B, J_{AB} = 10.2 Hz, 1 H), 3.48 (A*B*, J_{AB} = 10.2 Hz, 1 H), 4.58 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.8 (d), 28.1 (d), 31.4 (t), 35.6 (t), 37.1 (t), 37.2 (d), 37.8 (s), 38.0 (t), 40.9 (t), 46.1 (t), 65.6 (d) ppm. Exact mass (EI-HRMS): $C_{11}H_{16}Br_2$: calcd. 305.961323, found 305.963949.

General Procedure for Reactions of 1, 2, and 3 with Sodium: Granulated Na metal (70 mg, 3.0 mmol) was washed three times with pentane and was then placed in a stream of dry N_2 to evaporate residual pentane. The solvent (toluene or tetraglyme, 1 mL) was added, and the resulting suspension was heated with stirring under N_2 to 105 °C, whereupon a solution of the dihalide (**1**, **2** or **3**; 0.5 mmol) in toluene (1.5 mL) was added dropwise with stirring for 15 min. After all of the dihalide had been added, stirring of the reaction mixture was continued at 105 °C for 0.5 h. The reaction mixture was then cooled gradually to ambient temperature and was transferred to a flask by a cannula. The material thereby obtained was subjected to GLC analysis by using a capillary column (DB-210), which was maintained at 90 °C for 3 min and then was temperature-programmed from 90 to 180 °C at a rate of 10 °C/min (see Table 1). The material was further purified by vacuum transfer followed by column chromatography on alumina (activity grade I) with pentane elution. Whereas this procedure could be used to separate products **5** and **6**, we observed that **4** decomposed during chromatographic workup due to its instability toward alumina.[12]

General Procedure for the Reactions of 1 and 2 with Alkyllithium: A solution of **1** or **2** (0.5 mmol) in Et_2O (5 mL) under N_2 was cooled to −78 °C by using an external dry-ice/acetone cold bath. A pentane solution of the alkyllithium reagent (0.5 mmol) was added gradually with vigorous stirring to this cold solution. After the addition of RLi had been completed, the reaction mixture was warmed to −30 °C, and the reaction mixture was stirred at this temperature for 2 h. At that time, the external cold bath was removed, and the reaction mixture was warmed gradually to ambient temperature while stirring for 2 h. The reaction mixture was then poured into water (10 mL) with vigorous stirring, and the resulting aqueous suspension was extracted with pentane (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and filtered, and the filtrate was analyzed by GLC by using a capillary column (DB-210), which was maintained at 90 °C for 3 min and was then temperature-programmed from 90 to 180 °C at a rate of 10 °C/min. The results thereby obtained are shown in Table 2.

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[20] Authentic **8** was prepared by chlorination of 1-methyl-2-adamantanol[21b] by using the Ph_3P/CCl_4 reagent. IR (KBr): $\tilde{\nu}$ = 2920 (s), 2850 (m), 1450 (m), 900 (m), 770 cm^{-1} (m). ^1H NMR (C_6D_6): δ = 0.90 (s, 3 H), 0.92−2.40 (m, 13 H), 3.82 (br. s, 1 H) ppm. ^{13}C NMR (C_6D_6): δ = 28.6 (q), 29.1 (t), 30.9 (t), 35.6 (s), 37.5 (t), 38.0 (d), 38.4 (d), 45.8 (d), 74.3 (d) ppm.

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