Reaction of polyspirocyclic internal *gem* dibromocyclopropanes with methyllithium. An unusual carbenoid rearrangement

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Dedicated to Professor Irina P. Beletskaya on the occasion of her 75th birthday

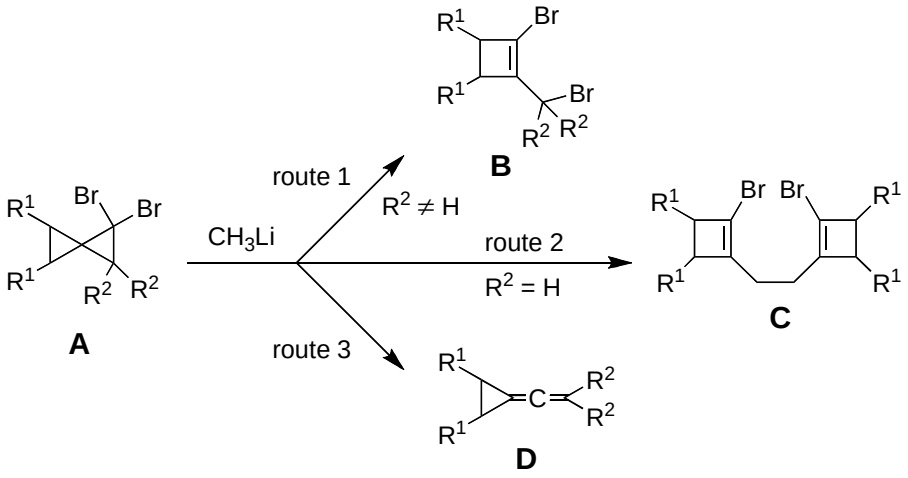
Abstract

A skeletal rearrangement of a series of polyspiro internal *gem* dibromocyclopropanes in the presence of methyllithium reagents was studied. The rearranged products of two types were obtained: substituted bromocyclobutenes (type **B**) and C-H insertion products (type **K**) resulting from the reaction of the carbenoid intermediate **H** with the ether solvent. The mechanism of the carbenoid rearrangement is discussed.

Keywords: *gem*-Dihalogenospiropentanes, carbenoid rearrangement, alkyllithium reagents, methylenecyclobuthylidene

Introduction

Earlier we have reported[1] the first example of a skeletal rearrangement of dibromospiranes of type **A** in the presence of methyllithium (Scheme 1, routes 1 and 2). In general, the reaction of dibromides **A** with methyllithium forms the corresponding allenes **D** as major products (Scheme 1, route 3). This transformation, so-called Doering-Scattebol-Moore reaction, is well documented.[2] It has been found that lowering the reaction temperature to –55 °C favors the formation of rearrangment products **B** and **C** and disfavors the formation of allenes **D**.[3]



Scheme 1

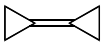
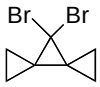
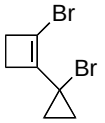
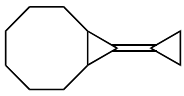
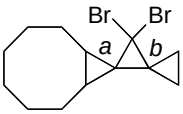
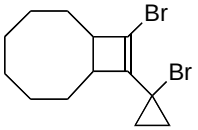
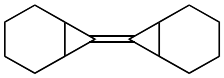
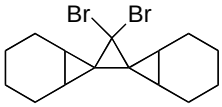
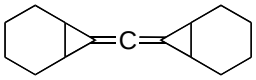
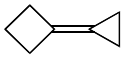
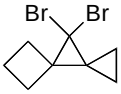
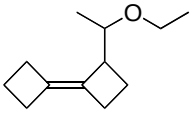
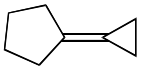
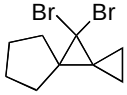
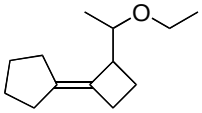
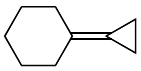
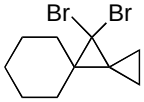
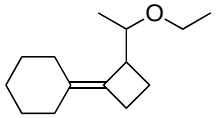
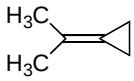
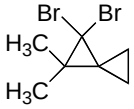
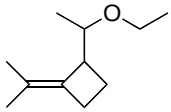
In our recent work[4] we have systematically studied the reaction of a number of terminal *gem* dibromospiropentanes with methyllithium forming dimer rearrangement products of type **C** (Scheme 1) in good yields. We have also investigated the reaction of several dibromospiranes containing tetrasubstituted dibromocyclopropane moieties with methyllithium, and either monomer rearrangement products **B** or C-H insertion products were obtained. Carbenes, including cyclopropylidene, can form molecules resulting from intramolecular insertion into C-H bonds of the solvent.[3c,5] In order to elucidate the mechanism a series of internal dibromospiropentanes have been studied in the reaction with methyllithium.

Results and Discussion

In the present work we explore the reaction of methyllithium with a series of *gem* dibromospiranes containing an internal *gem* dibromocyclopropane scaffold, with the goal to understand the influence of dibromocyclopropane substituents on the type of rearrangement products formed and to draw some conclusions about the mechanism of the rearrangement.

We synthesized *gem* dibromospiropentanes **1–7** (Table 1) by [1+2]-cycloaddition of dibromocarbene to a series of olefins and we studied the reactions of substrates **1–7** with methyllithium at low temperature (–55 °C). The results are summarized in Table 1.

Table 1. Substituted *gem* dibromospiropentanes **1**–**7** and rearrangement products **8**–**14** upon reaction with methyllithium

Olefin	Dibromospiropentane	Yield [%]	Rearrangement product	Yield [%]
	**1** 	79	**8** 	77
	**2** 	44	**9** 	70
	**3** 	71	**10** 	90
	**4** 	42	**11** 	58
	**5** 	32	**12** 	38
	**6** 	76	**13** 	89
	**7** 	49	**14** 	49

The first group of compounds **1**–**3** contains the 7,7-dibromodispiro[2.1.0]heptane moiety. Earlier, we have found that **1** reacts with methyllithium at –55 °C to produce mainly the monomer rearrangement product of type **B** (Scheme 1).[1] Repeating this reaction confirmed the formation of cyclobutene **8** in high yield (77%). The more substituted compound **2** reacted with methyllithium in the same manner yielding the rearranged product **9**. Dibromide **2** contains two bonds *a* and *b* prone to migrate. The formation of product **9** indicates that this rearrangement proceeds with migration of bond *a*, i.e., ring-opening of the more substituted three-membered ring occurs.

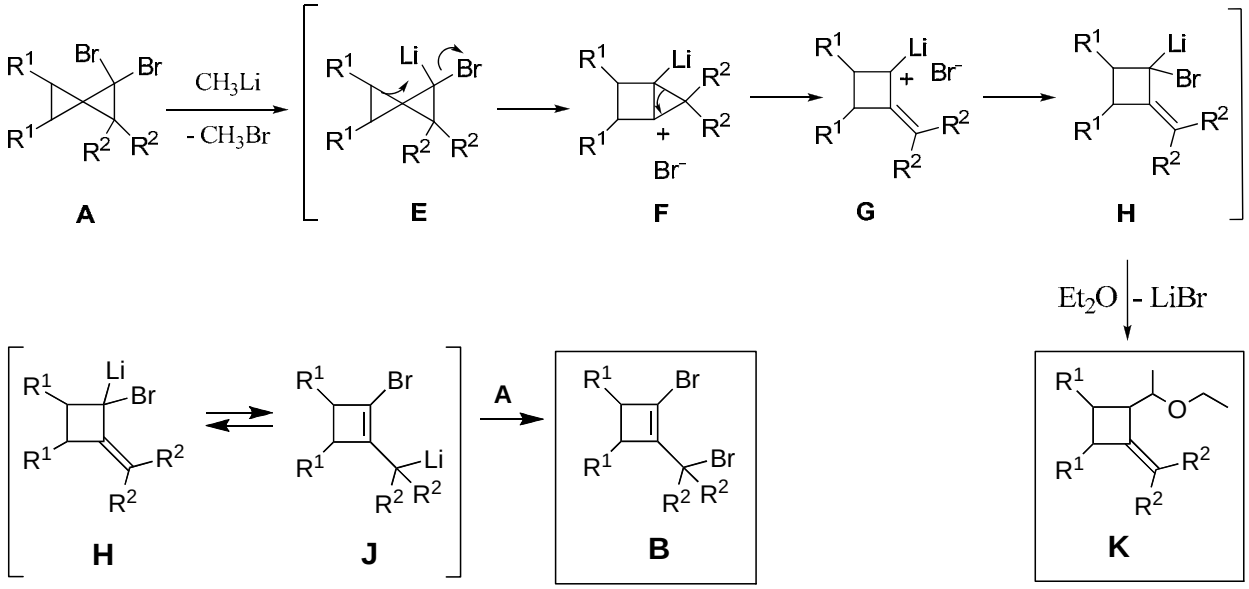
A different result was obtained with the tetrasubstituted dibromospiropentane **3.** Instead of a monomer product of type **B** (Scheme 1), the reaction with methyllithium at -–55 °C resulted in the formation of allene **10** (product type **D**, Scheme 1).

The reaction of methyllithium with dibromospiropentanes **4**–**6** containing spirocyclies of larger ring sizes gave a different result: ethers **11**–**13** were formed in the course of the incorporation of the ether solvent molecule, likely *via* an intermediacy of a corresponding carbene and its insertion into C-H bond of ether. It has been reported[5b] that treatment of

dibromide **6** with methyllithium at –45 °C provides a mixture of eight products with compound **13** as the main product (40% yield). We reinvestigated this reaction at –55 °C and isolated exclusively the product **13** in high yield (89%).

Thus, depending on the size of the cyclic substituent in dibromides **1**–**6** two types of rearrangement products were obtained: monomer products **8** and **9** of type **B** (Scheme 1) from dibromides **1** and **2** containing cyclopropyl substituents, and solvent insertion products **11**–**14** in the case of dibromides **4**–**7** with alkyl or larger cycloalkyl substituents. Reaction paths for the formation of rearrangment products **8**–**14** are conceived as follows (Scheme 2):

Presumably, the first step of the reaction of dibromospiranes **A** with methyllithium leads to the formation of lithium carbenoid **E**. Subsequently, nucleophilic attack of the C–C bond of the spiro-linked three-membered ring at the carbenoid center generates via sequence **F** and **G** the rearranged cyclobutylidene carbenoid **H**. The electrophilicity of carbenoids has been studied and thoroughly reviewed.[6]



Scheme 2

Depending on the structure, carbenoid **H** may serve as intermediate for two ramified pathways (Scheme 2). One is the insertion reaction into the α-C–H bond of diethyl ether used as solvent affording products of type **K**. This insertion probably proceeds *via* the formation of the corresponding carbene, a substituted methylenecyclobutylidene.

The alternative transformation of carbenoid **H** is the [1,3]-sigmatropic migration of Li furnishing the lithium intermediate **J** followed by metal-halogen exchange and formation of the rearranged product of type **B** (Scheme 2).

In conclusion, we propose a mechanistic rationalization for the rearrangement, which allows to explain the competing processes. The main point of the suggested reaction paths (Scheme 2) is

the concept of a carbocationic type of transformation of Li-carbenoid intermediates. Especially noteworthy is that carbenoids of the Li-C-Br type can react with such a weak nucleophile like a C–C bond. This process, which is still a rare case, represents the skeletal carbocationic-type rearrangements in carbenoids.

Experimental Section

General Procedures. NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 and 100.62 MHz for ^{1}H and ^{13}C, respectively) at room temperature; chemical shifts δ were measured with reference to the solvent (^{1}H: $CDCl_3$, δ = 7.24 ppm; ^{13}C: $CDCl_3$, δ = 77.13 ppm). Mass spectra were taken on a Finnigan MAT 95 XL spectrometer (70 eV) using electron impact ionization (EI) and GC-MS coupling. Microanalyses were performed on a Carlo Erba 1106 instrument. Analytical thin layer chromatography (TLC) was carried out with Silufol silica gel plates (supported on aluminum); the detection was done by UV lamp (254 and 365 nm) and chemical staining (iodine vapour). Melting points were determined on a Electrothermal 9100 capillary apparatus. Column chromatography was performed using silica gel 60 (230–400 mesh, Merck). Petroleum ether used refers to the fraction boiling at 40–60 °C. All reagents except commercial products of satisfactory quality were purified by literature procedures prior to use. Starting compounds: bicyclopropylidene,[7] (1-methylethylidene)cyclopropane,[8] cyclopropylidenecyclohexane,[9] cyclopropylidenecyclo- pentane,[9] cyclopropylidenecyclobutane,[9] 9-cyclopropylidenebicyclo[6.1.0]nonane,[10] 7,7'-bis(bicyclo[4.1.0]heptan)-7(7')-ene[11] were synthesized by known procedures.

Substituted *gem* dibromospiropentanes 1–7. General procedure

A mixture of *t*-BuOK (4.6 g, 41 mmol) and olefin (21 mmol) in petroleum ether (20 mL) was stirred at 0 °C under argon, and a solution of bromoform (6.15 g, 2.2 mL, 25 mmol) in petroleum ether (5 mL) was added dropwise. After 20 min, the reaction mixture was allowed to slowly warm to room temperature and after 24–72 h was quenched with cold water (40 mL). The aqueous layer was extracted with Et_2O (3 × 20 mL), the organic layers were combined, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude dibromides **1**–**7** were purified by distillation or by column chromatography (silica gel, petroleum ether).

7,7-Dibromodispiro[2.0.2.1]heptane (1).[1a] The reaction mixture was stirred for 24 h. Colorless crystals (2.92 g, 79%); bp 75–76 °C (8 mm Hg); mp 71 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07–1.13 (m, 4H), 1.23–1.29 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2 (4 CH_2), 31.9 (2 C), 40.7 (CBr_2)**.**

3',3'-Dibromodispiro[bicyclo[6.1.0]nonane-9,1'-cyclopropane-2',1''-cyclopropane] (2).[4] The reaction mixture was stirred for 16 h. Colorless oil (0.44 g, 44%); R_f = 0.6 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.77–0.91 (m, 4H), 1.05–1.79 (m, 12H), 1.80–1.89 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.0 (2 CH_2), 23.8 (2 CH_2), 26.4 (2 CH_2), 27.7 (2 CH), 28.8 (2 CH_2),

29.7 (C), 31.9 (C), 41.5 (C). MS (EI, 70 eV): *m*/*z* (%) 336 (0.2), 334 (0.6), 332 (0.2) [M^+], 240 (30), 238 (60), 236 (32); 173 (40), 171 (44); 159 (35), 157 (33), 131 (58), 117 (58), 91 (100).

3',3'-Dibromodispiro[bicyclo[4.1.0]heptane-7,1'-cyclopropane-2',7''-bicyclo[4.1.0]heptane] (3).[12] The reaction mixture was stirred for 72 h. Colorless solid (1.77 g, 71%); mp 170 °C (hexane); R_f = 0.6 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34–1.41 (m, 8H), 1.47–1.56 (m, 4H), 1.68–1.72 (m, 4H), 1.98–2.07 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1 (4 CH_2), 22.3 (4 CH), 23.2 (4 CH_2), 40.9 (2 C), 48.1 (CBr_2). MS MALDI-TOF: *m*/*z* (%) 284 (4) [M^+].

8,8-Dibromodispiro[2.0.3.1]octane (4). The reaction mixture was stirred for 24 h. Colorless liquid (1.02 g, 42%); bp 60–64°C/15 mm Hg. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05–1.18 (m, 4H), 1.80–2.05 (m, 4H), 2.34–2.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6 (2 CH_2, *J* = 165 Hz), 14.1 (CH_2, *J* = 136 Hz), 27.3 (2 CH_2, *J* = 138 Hz), 35.9 (C), 38.2 (C), 46.2 (CBr_2). MS MALDI–TOF: *m/z* (%) 264 (3) [M^+]. Anal. calcd. for $C_8H_{10}Br_2$ (265.97): C, 36.30; H, 3.81. Found: C, 36.13; H. 3.79.

9,9-Dibromodispiro[2.0.4.1]nonane (5). The reaction mixture was stirred for 24 h. Colorless liquid (0.73 g, 32%); bp 49–50°C/1 mm Hg. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05–1.20 (m, 4H), 1.46–1.56 (m, 2H), 1.60–1.70 (m, 2H), 1.77–1.82 (m, 2H), 2.06–2.16 (m, 2H). ^{13}C NMR (100 MHz): δ 11.9 (2 CH_2), 27.1 (2 CH_2), 34.2 (2 CH_2), 36.7 (C), 40.34 (C), 48.4 (CBr_2). Anal. calcd. for $C_9H_{12}Br_2$ (279.00): C, 38.50; H, 4.43. Found: C, 38.61; H 4.32.

10,10-Dibromodispiro[2.0.5.1]decane (6).[5b] The reaction mixture was stirred for 48 h. Colorless solid (1.46 g, 76%); mp 49–50°C; R_f = 0.8 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98–1.05 (m, 2H), 1.11–1.17 (m, 2H), 1.33–1.62 (m, 6H), 1.67–1.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.9 (2 CH_2), 25.0 (2 CH_2), 25.6 (CH_2), 33.7 (2 CH_2), 33.7 (C), 35.3 (C), 49.6 (CBr_2). Anal. calcd. for $C_{10}H_{14}Br_2$ (294.03): C, 40.85; H, 4.80. Found: C, 40.59; H 5.01.

1,1-Dibromo-2,2-dimethylspiro[2.2]pentane (7). Reaction mixture was stirred for 36 h. Colorless liquid (0.21 g, 49%); R_f = 0.5 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04–1.09 (m, 2H), 1.10–1.15 (m, 2H), 1.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2 (2 CH_2, *J* = 165 Hz), 23.3 (2 CH_3, *J* = 128 Hz), 29.0 (C), 35.9 (C), 49.8 (CBr_2). Anal. calcd. for $C_7H_{10}Br_2$ (253.96): C, 33.07; H, 3.89. Found: C, 33.11; H 3.97.

Reaction of substituted *gem* dibromospiropentanes 1–7 with methyllithium. General procedure

To a stirred solution of *gem* dibromospiropentanes **1–7** (3.3 mmol) in Et_2O (10 mL) at –55 °C under argon was added dropwise over a period of 45 min methyllithium (2.75 mL of 1.6 M solution in Et_2O, 4.4 mmol). After 1 h, the resulting mixture was allowed to slowly warm to 0 °C and was then quenched with cold water (20 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL), the organic layers were combined, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude products were purified by column chromatography (silica gel, petroleum ether).

1-Bromo-2-(1-bromocyclopropyl)cyclobutene (8).[1a] Colorless liquid (0.66 g, 77%); R_f = 0.35 (petroleum ether). ^{1}H and ^{13}C NMR data of **12** match those reported.[1a]

9-Bromo-10-(1-bromocyclopropyl)bicyclo[6.2.0]dec-9-ene (9).[4] Colorless oil (0.39 g, 70%); R_f = 0.6 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82–0.91 (m, 2H), 1.05–1.16 (m, 2H), 1.18–1.81 (m, 11H), 2.03–2.11 (m, 1H), 2.72–2.78 (m, 1H), 2.86–2.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9 (*J* = 165 Hz, CH_2), 17.4 (*J* = 164 Hz, CH_2), 24.9 (CH_2), 25.3 (CH_2), 25.9 (CH_2), 26.3 (CH_2), 29.5 (CH_2), 29.7 (CBr), 29.8 (CH_2), 48.6 (*J* = 141 Hz, CH), 51.1 (*J* = 139 Hz, CH), 114.5 (C), 147.3 (C). MS (EI, 70 eV): *m/z* (%) 336 (1), 334 (2), 332 (1) [M^+]; 255 (10), 253 (10) [$(M-Br)^+$]; 174 (25), 173 (66), 159 (25), 145 (32), 131 (57), 117 (49), 105 (62), 91(92), 84 (81), 67 (75), 55 (76), 51 (69), 49 (100), 43 (65), 39 (95).

7,7'-Methanediylidenebisbicyclo[4.1.0]heptane (10). Colorless liquid (0.13 g, 90%); R_f = 0.4 (chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23–1.47 (m, 8H), 1.77–1.93 (m, 8H), 1.98–2.05 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9 (2 CH), 19.0 (2 CH), 21.1 (2 CH_2), 21.2 (2 CH_2), 23.3 (2 CH_2), 23.7 (2 CH_2), 89.4 (2 C), 173.65 (C). MS MALDI-TOF: *m/z* (%) 200 (3) ([M^+].

[2-(1-Ethoxyethyl)cyclobutylidene]cyclobutane (11). Colorless liquid (0.21 g, 58%); R_f = 0.6 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (d, *J* = 6.1 Hz, 3H, CH_3), 1.19 (t, *J* = 6.9 Hz, 3H, CH_3), 1.67–2.75 (m, 10H), 3.01–3.09 (m, 1H, CH), 3.44–3.54 (m, 3H, CH_2O, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7 (CH_3), 16.2 (CH_3), 17.4 (CH_2), 19.4 (CH_2), 26.2 (CH_2), 29.2 (CH_2), 29.7 (CH_2), 47.6 (CH), 63.75 (CH_2O), 77.01 (CHO), 126.27 (C), 128.31 (C). MS (EI, 70 eV): *m/z* (%) 181 (1) [$(M+1)^+$], 164 (5), 138 (7), 137 (13), 123 (6), 122 (8), 121 (5), 109 (8), 108 (6), 95 (10), 93 (9), 81 (5), 79 (8), 73 (100), 45 (46), 41 (11), 29 (5).

[2-(1-Ethoxyethyl)cyclobutylidene]cyclopentane (12). Colorless liquid (0.34 g, 38%); R_f = 0.6 (petroleum ether). ^{1}H NMR δ 1.14 (d, *J* = 6.2 Hz, 3H, CH_3), 1.18 (t, *J* = 6.9 Hz, 3H, CH_3), 1.45–2.60 (m, 12H), 3.08–3.16 (m, 1H, CH), 3.39–3.48 (m, 1H, CH_2O), 3.50–3.65 (m, 3H, CH_2O, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7 (CH_3), 15.9 (CH_3), 18.8 (CH_2), 26.3 (CH_2), 26.9 (CH_2), 27.8 (CH_2), 29.5 (CH_2), 29.9 (CH_2), 47.7 (CH), 63.8 (CH_2O), 76.4 (CHO), 129.9 (C), 134.7 (C). MS (EI, 70 eV): *m/z* (%) 194 (1) [M^+], 148 (18), 133 (12), 119 (6), 105 (10), 91 (20), 79 (14), 73 (100), 67 (9), 45 (64), 43 (10), 29 (3).

[2-(1-Ethoxyethyl)cyclobutylidene]cyclohexane (13).[5b] Colorless liquid (0.61 g, 89%); R_f = 0.7 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (t, *J* = 6.6 Hz, 3H, CH_3), 1.19 (d, *J* = 6.0 Hz, 3H, CH_3), 1.39–1.53 (m, 6H), 1.61–1.76 (m, 2H), 1.88–1.94 (m, 2H), 1.99–2.07 (m, 2H), 2.40–2.56 (m, 2H), 3.14–3.22 (m, 1H, CH), 3.39–3.53 (m, 2H, CH_2O), 3.53–3.61 (m, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7 (*J* = 126 Hz, CH_3), 15.9 (*J* = 126 Hz. CH_3), 17.8 (*J* = 136 Hz, CH_2), 26.6 (CH_2), 26.8 (CH_2), 27.6 (CH_2), 27.7 (CH_2), 26.2 (CH_2), 29.7 (CH_2), 46.3 (*J* = 134 Hz, CH), 63.9 (*J* = 140 Hz, CH_2O), 76.6 (*J* = 139 Hz, CHO,, 129.4 (C), 131.9 (C). MS (EI, 70 eV): *m/z* (%) 209 (1) [$(M+1)^+$], 208 (1) [M^+], 207 (1) [$(M-1)^+$], 179 (2), 149 (65), 134 (13), 133 (22), 121 (44), 107 (68), 93 (70), 81 (78), 73 (100), 67 (73), 55 (80), 45 (96).

1-(1-Ethoxyethyl)-2-(1-methylethylidene)cyclobutane (14). Colorless liquid (0.13 g, 49%); R_f = 0.7 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (d, *J* = 6.3 Hz, 3H, CH_3), 1.18 (t, *J* = 7.1 Hz, 3H, CH_3), 1.49 (br s, 3H, CH_3), 1.58 (br s, 3H, CH_3), 1.65–1.69 (m, 1H, CH_2), 1.92–

1.97 (m, 1H, CH_2), 2.40–2.56 (br m, 2H, CH_2), 3.09–3.17 (br m, 1H, CH), 3.40–3.62 (m, 3H, CH_2O, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7 (*J* = 125 Hz, CH_3), 16.0 (*J* = 126 Hz, CH_3), 17.7 (*J* = 137 Hz, CH_2), 27.2 (*J* = 127 Hz, CH_3), 27.4 (*J* = 135 Hz, CH_2), 28.7 (*J* = 127 Hz, CH_3), 46.8 (*J* = 136 Hz, CH), 63.9 (*J* = 138 Hz, CH_2O), 76.6 (*J* = 144 Hz, CHO), 123.8 (C), 132.8 (C). MS (EI, 70 eV): *m/z* (%) 168 (1) [$(M+1)^+$], 124 (6), 107 (6), 95 (4), 91 (4), 81 (7), 73 (100), 67 (8), 55 (6), 45 (94), 41 (8), 29 (6).

Acknowledgements

We thank the Division of Chemistry and Materials Science RAS (Program № 1) and the President`s grant "Support of Leading Scientific School" N 2552.2006.3 (academician N.S. Zefirov) for financial support of this work.

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