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Carbenoid Rearrangement in the Series of Substituted *gem*-Dibromospiropentanes

K. N. Sedenkova, E. B. Averina, Yu. K. Grishin, T. S. Kuznetsova, and N. S. Zefirov

Lomonosov Moscow State University, Moscow, 119992 Russia
e-mail: elaver@org.chem.msu.ru

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Abstract—A series of new substituted *gem*-dibromospiropentanes was studied in a reaction with methyllithium at –55...–50°C. This reaction is a carbenoid rearrangement that leads to the formation of monomeric and dimeric bromocyclobutenes and also to the products of cyclobutylidene insertion into a C–H bond of the solvent depending on the character of substituents in the dibromospiropentane fragment.

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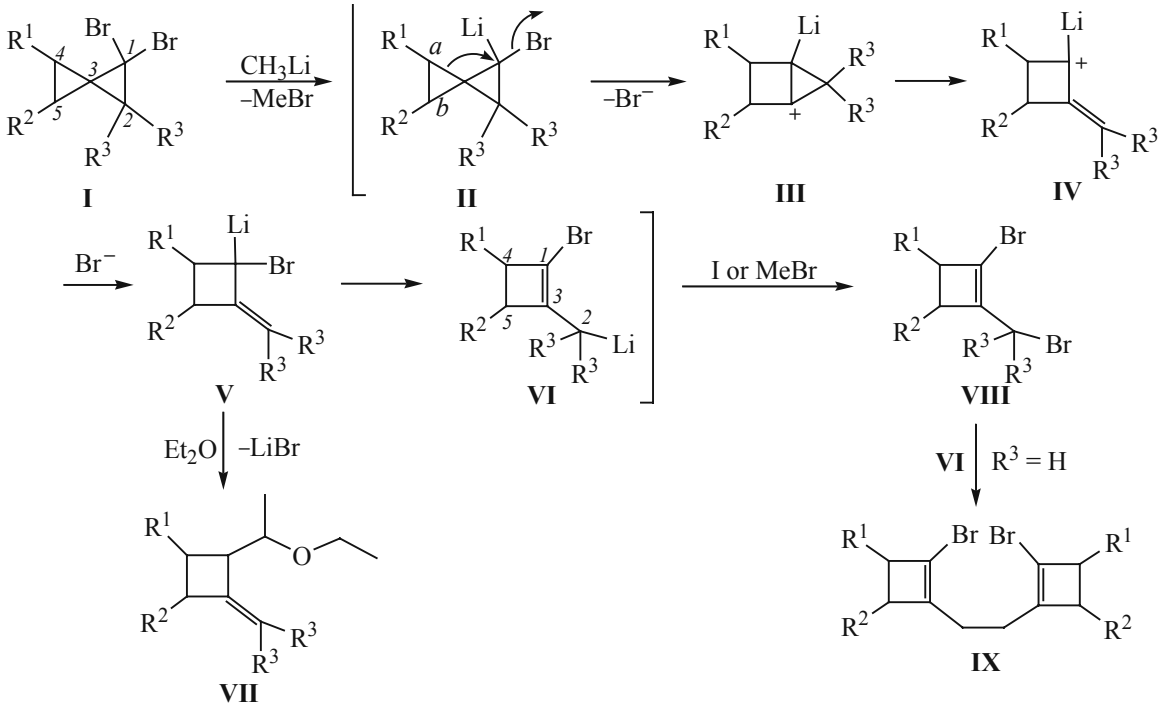
We formerly found that some *gem*-dibromo-substituted spiropentanes abnormally reacted with alkyllithium reagents: Depending on the conditions alongside the expected allenes products were obtained resulted from an uncommon dibromotriangulane rearrangement, monomeric or dimeric bromocyclobutenes [1–3]. Based on the experimental findings obtained [4] and also on the known data on the reaction of dihalocyclopropanes with alkyllitium reagents [5, 6] we suggested a general scheme of the reaction between dibromospiropentanes and methyllithium (Scheme 1).

In keeping with this scheme the key stage of the rearrangement is the reaction of dibromide **I** with methyllithium leading to a lithium derivative **II** followed

Scheme 1.



by a nucleophilic attack of the C–C bond of the three-membered ring on the carbenoid center with the formation of the corresponding cyclobutylidene intermediate **V** that can further either insert into the C–H bond of the solvent giving ether **VII** or isomerize into intermediate **VI**, a precursor of compounds **VIII** and **IX**. In the case of an unsym-metrically substituted dibromospiropentane **I** a migration of the bond *a* or *b* to the carbenoid center may occur with the formation of regioisomers of compounds **VIII** and **IX**.

Apparently the character of substituents in the spiropentane moiety governs the reaction pathway, the formation of rearrangement products or the insertion into the C–H bond of the solvent. Therefore a number of problems arises concerning the relationships in the dibromotriangulane rearrangement whose solution requires additional experimental research. In this connection we report here on the investigation of the reaction with methyllithium of a series of new substituted *gem*-dibromospiropentanes containing a terminal or internal dibromocyclopropane fragment.

By the reaction of [1+2]-cycloaddition of dibromocarbene to alkenes of methylenecyclopropane series **X–XVII** along the Doering–Hoffmann procedure [7] we prepared in fair yields the corresponding dibromospiropentanes **XVIII–XXV** (Scheme 2).

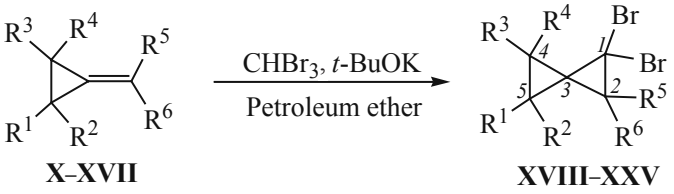
The reaction of *gem*-dibromospiropentanes with methyllithium was carried out in ether at –55...–50°C for just in these conditions the maximum yield of rearrangement products compared to allenes was attained as we had established before [4].

In reaction with methyllithium of dibromides **XVIII–XX** as expected the main reaction products were dimeric bromocyclobutenes **XXVI–XXVIII** (Scheme 3).

Compounds **XXVI–XXVIII** can form as two possible regioisomers with substituents in positions *3* or *4* of the cyclobutene ring. Besides the molecules of rearrangement products **XXVI** and **XXVII** contain each two asymmetric centers therefore each of these compounds should exist as a mixture of two diastereomers. According to the spectral data the formation of dimeric bromocyclobutenes **XXVI** and **XXVIII** occurred regioselectively, and compound **XXVII** was obtained as a mixture of four isomers.

In the ^{13}C NMR spectrum of dimer **XXVI** two sets of signals were observed with very close chemical shift values ($\Delta\delta$ 0.04–0.18 ppm). Consequently, compound

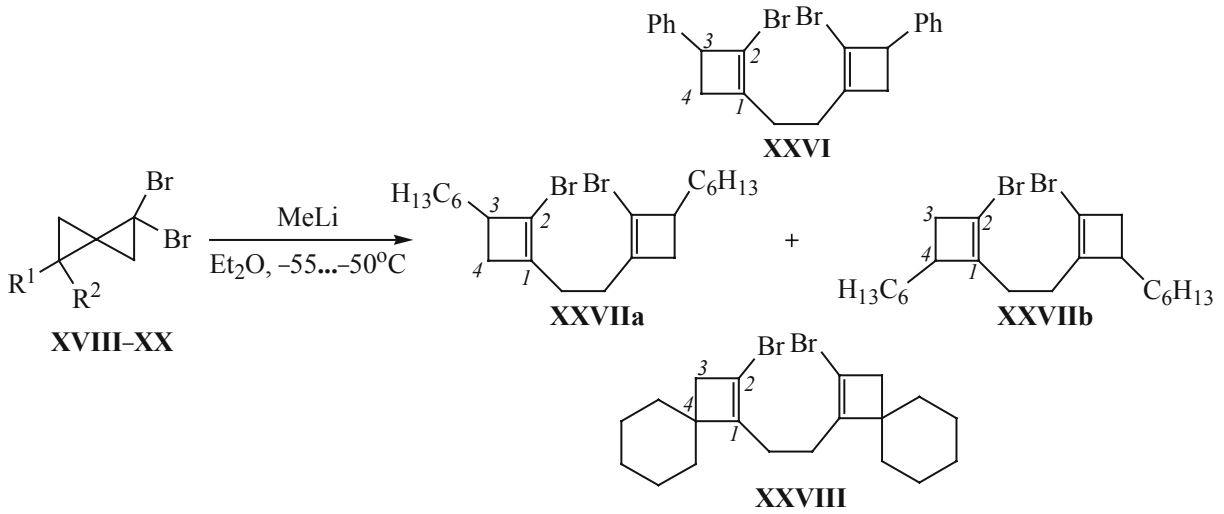
Scheme 2.



X–XVII **XVIII–XXV**

$R^2 = R^3 = R^4 = R^5 = R^6 = H$, R^1 = Ph (**X, XVIII**), *n*-C_6H_{13} (**XI, XIX**); $R^1,R^2 = (CH_2)_5$, $R^3 = R^4 = R^5 = R^6 = H$ (**XII, XX**); $R^1 = R^2 = R^3 = R^4 = H$, $R^5,R^6 = (CH_2)_5$ (**XIII, XXI**), $(CH_2)_4$ (**XIV, XXII**), $(CH_2)_3$ (**XV, XXIII**), $(CH_2)_2$ (**XVI, XXIV**); $R^1,R^3 = (CH_2)_4$, $R^2 = R^4 = H$, R^5,R^6 = spirobicyclo[4.0.1]heptane (**XVII, XXV**).

Scheme 3.



XXVI formed as one of two possible regioisomers that was a mixture of two diastereomers in an approximately equal ratio. The NMR spectra of compound **XXVI** did not permit the establishment what regioisomer formed in the reaction of dibromospiropentane **XVIII** with methyllithium, therefore we converted dibromide **XXVI** into the corresponding hydrocarbon **XXIX** by the use of a known reduction system lithium–*t*-BuOH [8, 9]. It was established by NOE experiment (Scheme 4) that in molecule **XXIX** the proton at the double bond is contiguous to the proton in the CHPh moiety. The additional confirmation of the formation of 3-phenyl-substituted regioisomer **XXVI** was the considerable upfield shift of proton and carbon signals of the CHPh group in the spectra of reduction product **XXIX** compared to the spectra of initial dibromide **XXVI** ($\Delta\delta_H$ ~0.2, and $\Delta\delta_C$ ~7.5 ppm respectively). The signals of carbon atoms from the methylene groups of the cyclobutene fragment have close values of the chemical shifts both in dibromide **XXVI** (δ 40.4 and 40.5 ppm) and hydrocarbon **XXIX** (δ 40.9 ppm).

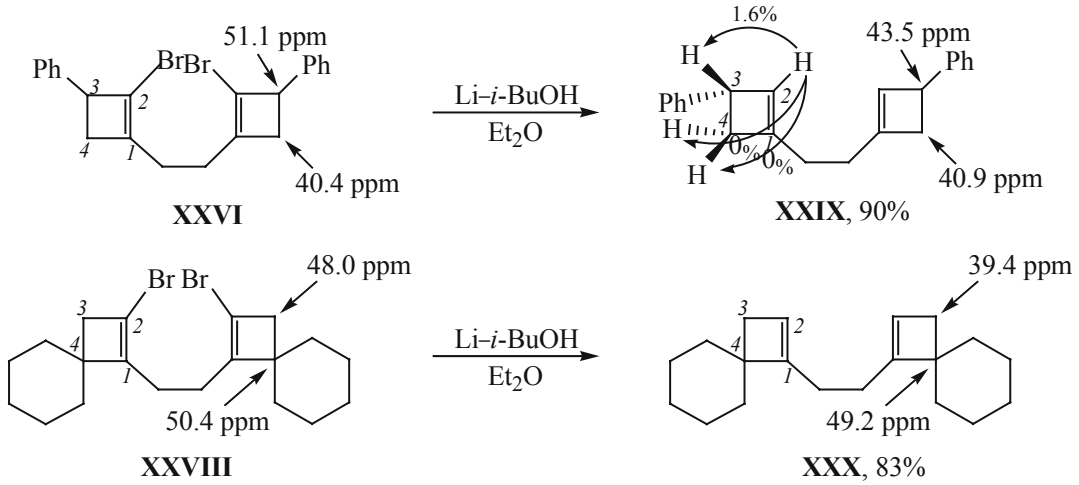
As was shown in [4], dimer **XXVIII** formed as a single regioisomer. To establish the substituent position in the cyclobutene ring we reduced dibromide **XXVIII** into hydrocarbon **XXX**. In favor of the formation of regioisomer **XXVIII** substituted in the position *4* testified the considerable upfield shift in the ^{13}C NMR spectrum of hydrocarbon **XXX** of the carbon signal belonging to the CH_2 group of the cyclobutene (δ 39.4 ppm) compared to the spectrum of dibromide **XXVIII** (δ 48.0 ppm); therewith the chemical shifts of the quaternary carbon atoms in the spectra of compounds **XXVIII** and **XXX** had similar values (δ 50.4 and 49.2 ppm respectively).

Hence in the reaction of phenyl-substituted dibromospiropentane **X** with methyllithium rearrangement product **XXVI** formed through a migration to the carbenoid center of intermediate **II** of the more substituted bond *a* (Scheme 1). In the case of dispirocompound **XII** the bond *b* migrates to the carbenoid center leading to the formation of regioisomer **XXVIII** substituted in the position *4*. According to NMR spectra the reaction of dibromospiropentane **XI** with methyllithium was nonselective: The formed dimeric bromocyclobutene **XXVII** was a mixture of two regioisomers each of which contained two diastereomers.

We presumed that the presence in the initial dibromospiropentanes of substituents stabilizing the transition state in the course of the formation of intermediate **III** should favor the migration of the more substituted bond to the carbenoid center of intermediate **II** as was really observed with dibromide **XVIII**. However it turned out that with the growing bulk of the substituent the reaction pathway was strongly affected by steric factors; as a result either a regioisomers mixture formed (reaction of dibromide **XIX** with methyllithium), or the regiodirection was totally changed (reaction of dibromide **XX** with methyllithium).

As shown in Scheme 1 the reaction of internal dibromospiropentans with methyllithium led to the formation of monomeric products of dibromotriangulane rearrangement **VIII** or to the products of insertion into the C–H bond of the solvent **VII**. To reveal the effect of the volume of cyclic substituents in the spiropentane fragment on the direction of the reaction we studied the reaction with methyllithium of a series of polycyclic dibromides **XXI–XXIV**.

Scheme 4.



XXVI **XXIX**, 90%

XXVIII **XXX**, 83%

It proved that dibromides **XXI–XXIII** notwithstanding the size of the substituent in the three-membered ring provided in the reaction with methyllithium exclusively the products of cyclobutylidene insertion into the C–H bond of ether (Scheme 5), whereas from dibromide **XXIV** formed solely substituted bromocyclobutene **XXXIV**. Inasmuch as the difference in the bulk of substituents in the spiropentane fragment of dibromides **XXIII** and **XXIV** was insignificant, it was possible to expect in the reaction of compound **XXIV** with methyllithium a formation of a mixture of substances **VII** and **VIII**. However the analysis of the NMR spectra of the reaction mixture showed that the treatment of dibromodispiroheptane **XXIV** with methyllithium resulted in the formation in a high yield of a single reaction product, monomeric bromocyclobutene **XXXIV** in agreement with the data of [1].

An unexpected result was obtained in the reaction of tetra-substituted dibromodispiroheptane **XXV** with methyllithium (Scheme 6): Instead of monomeric bromocyclobutene **VIII** or insertion product **VII** in this reaction formed in a good yield even at –60°C exclusively allene **XXXV** apparently because the isomerization of intermediate **II** into cyclobutylidene **V** was impossible due to steric factors.

The results obtained are consistent with the general scheme of reaction between dibromospiropentanes with methyllithium (Scheme 1) and indirectly confirm the existence of intermediates **II–VI**.

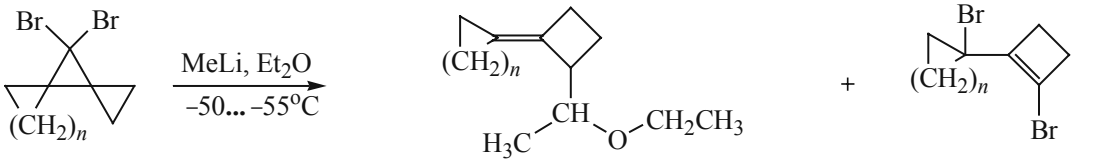
Evidently the dibromotriangulane rearrangement under study possesses a carbocationic character and is a rare example of the manifestation of the electrophilic nature of the bromolithium carbenoids of the spiropentane structure. In the most events the carbene carbon atom of intermediate **II** is subjected to the nucleophilic attack of the C–C bond resulting in the formation of cyclobutylidene carbenoid **V** that further depending on the bulk and apparently on the electronic character of the substituents may either insert into the C–H bonds of the solvent or undergo a [1,3]-sigmatropic migration of the C–Li bond giving intermediate **VI**. It is also evident that if in the course of the rearrangement the energy of intermediates **III** and **IV** increases due to the growing structural strain (reaction of dibromide **XXV** with methyllithium) carbenoid **II** is stabilized by allene formation.

Thus the data on the reaction of dihalospiropentanes with methyllithium demonstrate the dual nature of lithium carbenoids of the polyspirocyclopropane structure that can react not only with electrophilic reagents (traditional path) but also with nucleophiles, even so weak as the C–C bond.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance-400 at operating frequencies 400 and 100 MHz respectively from solutions of compounds

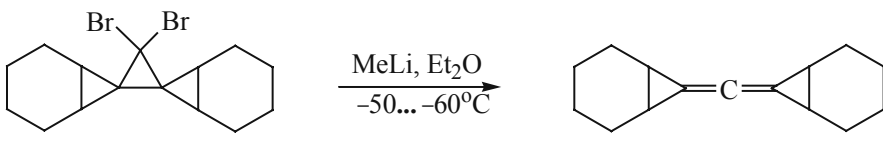
Scheme 5.



XIII–XVI **XXXI** (89%), **XXXII** (30%), **XXXIII** (58%) **XXXIV** (70%)

n = 4 (**XIII, XXXI**), 3 (**XIV, XXXII**), 2 (**XV, XXXIII**), 1 (**XVI, XXXIV**).

Scheme 6.



XXV **XXXV**, 60%

in $CDCl_3$. The chloroform signal (δ_H 7.24, δ_C 77.10 ppm) served as internal reference.

Mass spectra were obtained on an instrument MS Finnigan MAT ITD-700 at the energy of ionizing electrons 70 eV. Mass spectra MALDI of positive ions were recorded on a mass spectrometer Bruker Daltonics Ultraflex using as a matrix 1,8,9-trihydroxyanthracene.

The progress of reactions was monitored and the purity of the chemical substances was checked by TLC on Silufol UV-254 plates. In the preparative column chromatography silica gel Merck 40/60 was used. GLC analyses were carried out on a chromatograph Chrom-5 equipped with a flame-ionization detector, column 3000×5 mm, stationary phase 10% SE-30, operating temperature range 130–180°C. The preparative separation of low-boiling compounds was performed on a PAKhV-08 device equipped with a katharometer as a detector, column 3000×5 mm, stationary phase 15% E-301 on Inerton AW, carrier gas helium, flow rate 80–120 ml/min.

Bicyclopropylidene **XXIV** was synthesized by procedure [10]. Initial alkenes **XVIII–XX** were obtained by methods [11–14], compounds **XXI–XXIII**, by [15–17], alkene **XXV**, by [18, 19].

Addition of dibromocarbene to olefins X–XVII. To 4.6 g (41 mmol) of *t*-BuOK and 21 mmol of olefin in 20 ml of petroleum ether while stirring and cooling to 0°C was added 6.15 g (2.2 ml, 25 mmol) of bromoform. Then the reaction mixture was warmed to room temperature, and the stirring was continued for 17–72 h. The reaction mixture was treated with an equal volume of ice water, the organic layer was separated, and the products were extracted from the water layer into ether (3×20 ml). The combined organic extracts were washed with water (3×20 ml) and dried with $MgSO_4$. The solvent was distilled off, the residue was distilled in a vacuum or subjected to chromatography.

1,1-Dibromo-4-phenylspiro[2.2]pentane (XVIII) [20]. The reaction mixture was stirred for 18 h. Yield 52%, bp 120°C (5 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.65 d.d (1H, CH_2, ^2J 5.3, ^3J 6.1 Hz), 1.91 d.d (1H, CH_2, ^2J 5.3, ^3J 8.8 Hz), 1.94 d (1H, CH_2, ^2J 6.7 Hz), 2.11 d (1H, CH_2, ^2J 6.7 Hz), 2.71 d.d (1H, CH, ^3J 6.1, ^3J 8.8 Hz), 7.14 d (2H, H^o, ^3J 7.6 Hz), 7.25–7.29 m (1H, H^p), 7.32–7.38 m (2H, H^m). ^{13}C NMR spectrum, δ, ppm: 20.29 (CH_2), 27.76 (CH_2), 28.04 (CH, *cyclo*-Pr), 29.72 (C_{spiro}), 35.52 (CBr_2), 126.45 (2CH, Ph), 126.51 (CH, Ph), 128.54 (2CH, Ph), 139.50 (C, Ph).

1,1-Dibromo-4-hexylspiro[2.2]pentane (XIX). The reaction mixture was stirred for 20 h. Yield 52%, R_f 0.8 (petroleum ether). ^{1}H NMR spectrum, δ, ppm: 0.88–0.92 m (3H, CH_3), 0.98 d.d (1H, CH_2, *cyclo*-Pr, ^2J 6.2, ^3J 5.6 Hz), 1.26–1.40 m (11H, *cyclo*-Pr + hexane), 1.49 d.d (1H, *cyclo*-Pr, ^3J 5.6, ^3J 8.0 Hz), 1.89 d (1H, CH_2, *cyclo*-Pr, ^2J 6.4 Hz), 1.96 d (1H, CH_2, *cyclo*-Pr, ^2J 6.4 Hz). ^{13}C NMR spectrum, δ, ppm: 14.10 (CH_3, $^1J_{CH}$ 124 Hz), 17.94 (CH_2, *cyclo*-Pr, $^1J_{CH}$ 163 Hz), 22.64 (CH_2, $^1J_{CH}$ 126 Hz), 23.82 (CH, $^1J_{CH}$ 163 Hz), 27.12 (CH_2, *cyclo*-Pr, $^1J_{CH}$ 165 Hz), 28.64 (CH_2, $^1J_{CH}$ 126 Hz), 29.09 (CH_2, $^1J_{CH}$ 124 Hz), 30.86 (C_{spiro}), 31.78 (CH_2, $^1J_{CH}$ 122 Hz), 31.95 (CH_2, $^1J_{CH}$ 120 Hz), 33.07 (CBr_2). Found, %: C 42.32; H 6.10. $C_{11}H_{18}Br_2$. Calculated, %: C 42.61; H 5.85.

1,1-Dibromodispiro[2.0.5.1]decene (XX). The reaction mixture was stirred for 6 h. Yield 52%, bp 92–93°C (2 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.84 d (1H, *cyclo*-Pr, ^2J 4.5 Hz), 0.95 d (1H, *cyclo*-Pr, ^2J 4.5 Hz), 1.15–1.42 m (2H, cyclohexane), 1.43–1.68 m (6H, cyclohexane), 1.72–1.88 m (2H, cyclohexane), 1.80 d (1H, *cyclo*-Pr, ^2J 6.2 Hz), 1.92 d.d (1H, *cyclo*-Pr, ^2J 6.2, ^4J 0.8 Hz). ^{13}C NMR spectrum, δ, ppm: 22.76 (CH_2, *cyclo*-Pr), 25.27 (CH_2, cyclohexane), 25.70 (CH_2, cyclohexane), 26.01 (CH_2, cyclohexane), 27.70 (CH_2, *cyclo*-Pr), 30.36 (C_{spiro}), 32.24 (C_{spiro}), 32.32 (CH_2, cyclohexane), 33.99 (CH_2, cyclohexane), 36.19 (CBr_2). Found, %: C 40.87; H 4.75. $C_{10}H_{14}Br_2$. Calculated, %: C 40.82; H 4.76.

10,10-Dibromodispiro[2.0.5.1]decene (XXI) [21]. The reaction mixture was stirred for 48 h. Yield 76%, R_f 0.8 (petroleum ether), mp 49–50°C. ^{1}H NMR spectrum, δ, ppm: 0.98–1.05 m (2H, *cyclo*-Pr), 1.11–1.17 m (2H, *cyclo*-Pr), 1.33–1.62 m (6H, cyclohexane), 1.66–1.83 m (4H, cyclohexane). ^{13}C NMR spectrum, δ, ppm: 9.91 ($2CH_2$, *cyclo*-Pr), 24.98 ($2CH_2$, cyclohexane), 25.56 (CH_2, cyclohexane), 33.70 ($2CH_2$, cyclohexane), 33.73 (C_{spiro}), 35.33 (C_{spiro}), 49.56 (CBr_2).

9,9-Dibromodispiro[2.0.4.1]nonane (XXII). The reaction mixture was stirred for 23 h. Yield 32%, bp 49–50°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.05–1.20 m (4H, *cyclo*-Pr), 1.46–1.56 m (2H, cyclopentane), 1.60–1.70 m (2H, cyclopentane), 1.77–1.82 m (2H, cyclopentane), 2.06–2.16 m (2H, cyclopentane). ^{13}C NMR spectrum, δ, ppm: 11.92 ($2CH_2$, *cyclo*-Pr), 27.14 ($2CH_2$, cyclopentane), 34.17 ($2CH_2$, cyclopentane), 36.66 (C_{spiro}), 40.34 (C_{spiro}), 48.37 (CBr_2). Found %: C 38.50; H 4.43. $C_9H_{12}Br_2$. Calculated %: C 38.61; H 4.32.

8,8-Dibromodispiro[2.0.3.1]octane (XXIII). The reaction mixture was stirred for 24 h. Yield 42%, bp 60–64°C (15 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.05–1.18 m (4H, *cyclo*-Pr), 1.80–2.05 m (4H, *cyclo*-Bu), 2.34–2.49 m (2H, *cyclo*-Bu). ^{13}C NMR spectrum, δ, ppm: 11.59 ($2CH_2$, *cyclo*-Pr, $^1J_{CH}$ 165 Hz), 14.10 (CH_2, *cyclo*-Bu, $^1J_{CH}$ 136 Hz), 27.25 ($2CH_2$, *cyclo*-Bu, $^1J_{CH}$ 138 Hz), 35.85 (C_{spiro}), 38.18 (C_{spiro}), 46.17 (CBr_2). Mass spectrum MALDI-TOF: *m/z* 264 $[M]^+$. Found %: C 36.30; H 3.81. $C_8H_{10}Br_2$. Calculated %: C 36.13; H 3.79.

7,7-Dibromodispiro[2.0.2.1]heptane (XXIV) [22]. The reaction mixture was stirred for 24 h. Yield 79%, mp 70°C (from hexane). ^{1}H NMR spectrum, δ, ppm: 1.07–1.14 m (4H, *cyclo*-Pr), 1.23–1.27 m (4H, *cyclo*-Pr).

3',3'-Dibromodispiro(bicyclo[4.1.0]heptane-7,1'-cyclopropane-2',7''-bicyclo[4.1.0]heptane) (XXV) [23]. The reaction mixture was stirred for 72 h. Yield 71%. ^{1}H NMR spectrum, δ, ppm: 1.34–1.41 m (8H), 1.47–1.56 m (4H), 1.68–1.72 m (4H), 1.98–2.07 m (4H). Mass spectrum MALDI-TOF: *m/z* 284 $[M]^+$.

Reaction of *gem*-dibromocyclopropanes XVIII–XXV with methyllithium. To a solution of 5.1 mmol of dibromospiropentane in 10 ml of ether under an argon atmosphere was added at –55°C within 1 h 6.85 ml (7.6 mmol) of 1.5 N solution of methyllithium. The reaction mixture was warmed to 0°C and treated with an equal volume of ice water. The organic layer was separated, and the products were extracted from the water layer into ether (3 × 5 ml). The combined organic solution was washed with 10 ml of water and dried with $MgSO_4$. The solvent was distilled off, and the residue was purified by preparative column chromatography.

1,1'-[Ethane-1,2-diylbis(2-bromocyclobut-2-ene-3,1-diyl)]dibenzene (XXVI) was obtained as a mixture of two diastereomers A and B, 1.1:1. Yield 67%, R_f 0.1 (petroleum ether). ^{1}H NMR spectrum, δ, ppm, A+B: 2.51–2.53 m [6H, CH_2 (A) + 6H, CH_2 (B)], 3.10–3.11 m [(2H, CH_2, *cyclo*-Bu (A) + 2H, CH_2, *cyclo*-Bu (B)], 4.19 br.s [2H, CH, *cyclo*-Bu (A) + 2H, CH, *cyclo*-Bu (B)], 7.30–7.45 m [10H, Ph (A) + 10H, Ph (B)]. ^{13}C NMR spectrum, δ, ppm (A+B): 25.40 [CH_2, $^1J_{CH}$ 130 Hz (A)], 25.44 [CH_2, $^1J_{CH}$ 130 Hz (B)], 40.48 [$2CH_2$, *cyclo*-Bu, $^1J_{CH}$ 142 Hz (B)], 40.41 [$2CH_2$, *cyclo*-Bu, $^1J_{CH}$ 142 Hz (A)], 51.06 [2CH, $^1J_{CH}$ 143 Hz (A) + 2CH, $^1J_{CH}$ 143 Hz (B)], 113.44 [2CBr (B)], 113.48 [2CBr (A)], 126.96 (2CH, Ph), 127.01 (2CH, Ph), 127.09 [4CH, Ph (A)], 127.15 [2CH+2CH, Ph (A+B)], 128.67 [4CH+4CH, Ph (A+B)], 139.90 [2C, Ph (B)], 139.99 [2C, Ph (A)], 147.65 [2C= (B)], 147.78 [2C= (A)]. Found, %: C 59.65; H 4.80. $C_{22}H_{20}Br_2$. Calculated, %: C 59.49; H 4.54.

1,1'-Ethane-1,2-diylbis(2-bromo-3-hexylcyclobutene) (XXVIIa), 1,1'-ethane-1,2-diylbis(2-bromo-4-hexylcyclobutene) (XXVIIb).* Yield 77%, R_f 0.7 (petroleum ether). ^{1}H NMR spectrum, δ, ppm: 0.89–0.92 m (6H, $2CH_3$), 1.25–1.49 m (20H), 1.61–1.67 m (3H), 2.07–2.31 m (4H), 2.53–2.55 m (1H), 2.76–2.90 m (2H). ^{13}C NMR spectrum, δ, ppm: 14.08 (4 isomers, $2CH_3$), 22.63 (4 isomers, $2CH_2$); 24.25, 24.33, 24.24, 24.49 (4 isomers, $1CH_2$); 25.03 (CH_2), 25.08 (CH_2), 25.13 (CH_2); 26.66, 26.72, 26.79, 26.86 (4 isomers, CH_2), 27.56 ($2CH_2$); 29.40 (4 isomers, $2CH_2$), 29.70 (4 isomers, $2CH_2$), 31.80 (4 isomers, $2CH_2$); 32.32, 32.36, 32.47, 32.74 (4 isomers, CH_2); 36.14, 36.18, 36.25, 36.34 (4 isomers, CH_2); 41.74 ($2CH_2$), 43.54, 43.60, 43.37, 43.88 (4 isomers, CH); 47.07 (4 isomers, CH); 109.12 (2C=), 114.37 (C=), 114.43 (=C), 145.41 (2C=), 151.24 (C=), 151.32 (C=). Mass spectrum MALDI-TOF: *m/z* 460 $[M]^+$.

1,1'-Ethane-1,2-diylbis(2-bromospiro[3.5]non-1-ene (XXVIII). Yield 75%, R_f 0.6 (petroleum ether). ^{1}H NMR spectrum, δ, ppm: 1.09–1.24 m (2H), 1.25–1.41 m (4H), 1.44–1.77 m (14H), 2.23 s (4H), 2.47 s (4H). ^{13}C NMR spectrum, δ, ppm: 23.37 ($2CH_2$, $^1J_{CH}$ 130 Hz), 24.36 ($4CH_2$, $^1J_{CH}$ 123 Hz), 25.48 ($2CH_2$, $^1J_{CH}$ 119 Hz), 34.42 ($4CH_2$, $^1J_{CH}$ 124 Hz), 48.03 ($2CH_2$, *cyclo*-Bu, $^1J_{CH}$ 141 Hz), 50.40 ($2C_{spiro}$), 109.43 (2CBr=), 155.33 (2C=). Found, %: C 56.00; H 6.02. $C_{20}H_{28}Br_2$. Calculated, %: C 56.07; H 6.54.

[2-(1-Ethoxyethyl)cyclobutylidene]cyclohexane (XXXI) [21]. Yield 89%. ^{1}H NMR spectrum, δ, ppm: 1.15 d.d (3H, CH_3, ^3J 6.8, 6.3 Hz), 1.19 d (3H, CH_3, ^3J 5.5 Hz), 1.39–1.53 m (6H), 1.61–1.76 m (2H), 1.88–1.94 m (2H, *cyclo*-Bu), 1.99–2.07 m (2H, *cyclo*-Bu), 2.40–2.56 m (2H), 3.14–3.22 m (1H, CH, *cyclo*-Bu), 3.39–3.53 m (2H, CH_2O), 3.53–3.61 m (1H, CHO). ^{13}C NMR spectrum, δ, ppm: 15.65 (CH_3, $^1J_{CH}$ 126 Hz), 15.87 (CH_3, $^1J_{CH}$ 126 Hz), 17.84 (CH_2, *cyclo*-Bu, $^1J_{CH}$ 136 Hz), 26.59 (CH_2), 26.79 (CH_2), 27.57 (CH_2), 27.70 (CH_2), 29.19 (CH_2, cyclohexane, $^1J_{CH}$ 124 Hz), 29.68 (CH_2, cyclohexane, $^1J_{CH}$ 125 Hz), 46.26 (CH, *cyclo*-Bu, $^1J_{CH}$ 134 Hz), 63.88 (CH_2O, $^1J_{CH}$ 140 Hz), 76.58 (CHO, $^1J_{CH}$ 139 Hz), 129.35 (C=), 131.90 (C=). Mass spectrum, *m/z* (I_{rel}, %): 209 (2) $[M + 1]^+$, 208 (1)

* Compound **XXVII** was obtained as a mixture of two regioisomers at a ratio ~1:1, and each of them consisted of two diastereomers at a ratio ~1:1. Due to a large number of overlapping signals of aliphatic protons ^{1}H NMR spectrum is reported without assignment to isomers. In the ^{13}C NMR spectrum the signals of carbon atoms of four isomers are indicated without assignment to individual isomers.

$[M]^+$, 207 (1) $[M-1]^+$, 179 (2), 149 (65) $[M-CH_2OEt]^+$, 134 (13) $[M-Et_2O]^+$, 133 (22), 121 (44), 107 (68), 93 (70), 81 (78), 73 (100), 67 (73), 55 (80), 45 (96).

[2-(1-Ethoxyethyl)cyclobutylidene]cyclopentane (XXXII). Yield 30%. ^{1}H NMR spectrum, δ, ppm: 1.14 d (3H, CH_3, ^3J 6.7 Hz), 1.18 d.d (3H, CH_3, ^3J 7.0, 6.8 Hz), 1.45–2.60 m (12H), 3.08–3.16 m (1H, CH, *cyclo*-Bu), 3.39–3.48 m (1H, CH_2O), 3.50–3.65 m (1H, CH_2O + 1H, CHO). ^{13}C NMR spectrum, δ, ppm: 15.68 (CH_3), 15.93 (CH_3), 18.82 (CH_2), 26.28 (CH_2), 26.92 (CH_2), 27.84 (CH_2), 29.45 (CH_2), 29.91 (CH_2), 47.66 (CH, *cyclo*-Bu), 63.77 (CH_2O), 76.44 (CHO), 129.85 (C=), 134.71 (C=). Mass spectrum, *m/z* (I_{rel}, %): 194 (1) $[M]^+$, 148 (18) $[M-OEtH]^+$, 133 (12),119 (6), 105 (10), 91 (20), 79 (14), 73 (100) $[MeCH(OEt)]^+$, 67 (9), 45 (64), 43 (10), 29 (3).

[2-(1-Ethoxyethyl)cyclobutylidene]cyclobutane (XXXIII). Yield 58%. ^{1}H NMR spectrum, δ, ppm: 1.12 d (3H, CH_3, ^3J 6.1 Hz), 1.19 d.d (3H, CH_3, ^3J 7.1, 6.8 Hz), 1.67–2.75 m (10H), 3.01–3.09 m (1H, CH, *cyclo*-Bu), 3.44–3.54 m (3H, CH_2O + CHO). ^{13}C NMR spectrum, δ, ppm: 15.71 (CH_3), 16.17 (CH_3), 17.35 (CH_2), 19.42 (CH_2), 26.19 (CH_2), 29.24 (CH_2), 29.70 (CH_2), 47.62 (CH, *cyclo*-Bu), 63.75 (CH_2O), 77.01 (CHO), 126.27 (C=), 128.31 (C=). Mass spectrum, *m/z* (I_{rel}, %): 181 (1) $[M+1]^+$, 164 (5), 138 (7), 137 (13), 123 (6), 122 (8), 121 (5) $[M-CH_2OEt]^+$, 109 (8), 108 (6), 95 (10), 93 (9), 81 (5), 79 (8), 73 (100), 45 (46), 41 (11), 29 (5).

1-Bromo-2-(1-bromocyclopropyl)cyclobutene (XXXIV) [1]. Yield 77%, R_f 0.3 (petroleum ether). ^{1}H NMR spectrum, δ, ppm: 1.25–1.31 m (2H, CH_2, *cyclo*-Pr), 1.37–1.41 m (2H, CH_2, *cyclo*-Pr), 2.59–2.62 m (2H, CH_2, *cyclo*-Bu), 2.63–2.69 m (2H, CH_2, *cyclo*-Bu). ^{13}C NMR spectrum, δ, ppm: 16.16 ($2CH_2$, *cyclo*-Pr), 25.46 (CBr, *cyclo*-Pr), 30.59 (CH_2), 33.45 (CH_2), 108.23 (CBr=), 146.15 (C=).

7,7'-Methanediylidenebisbicyclo[4.1.0]heptane (XXXV). Yield 90%. ^{1}H NMR spectrum, δ, ppm: 1.23–1.47 m (8H), 1.77–1.93 m (8H), 1.98–2.05 m (4H). ^{13}C NMR spectrum, δ, ppm: 18.86 (2CH), 18.99 (2CH), 21.10 ($2CH_2$), 21.22 ($2CH_2$), 23.33 ($2CH_2$), 23.65 ($2CH_2$), 89.39 (2C=), 173.65 (=C=). Mass spectrum MALDI-TOF: *m/z* 200 $[M]^+$.

Reduction of dimeric bromocyclobutenes XXVI and XXVIII). To a solution of 0.16 mmol of dibromide and 1 ml (10.5 mmol) of *t*-BuOH in 100 ml of anhydrous ether at vigorous stirring while heating at reflux under an argon atmosphere was added by small portions (as needed) within five days 0.07 g (10.0 mmol) of lithium metal. Then the reaction mixture was quenched with 20 ml of ice water and extracted with ether (3×10 ml). The combined ether solution was washed with water (3×10 ml). The solvent was distilled off, and the residue was purified by preparative column chromatography.

1,1'-[Ethane-1,2-diylbis(cyclobut-2-ene-3,1-diyl)]-dibenzene (XXIX). Yield 90%, R_f 0.8 (petroleum ether). ^{1}H NMR spectrum, δ, ppm: 2.42 d (2H, CH_2, *cyclo*-Bu, ^2J 13.1 Hz), 2.44 br.s (4H, CH_2), 3.06 d.d (2H, CH_2, *cyclo*-Bu, ^2J 13.1, ^3J 4.5 Hz), 3.96 br.d (2H, 2CHPh, ^3J 4.5 Hz), 6.12 br.s (2H, 2CH=), 7.27–7.43 m (10H, 2Ph). ^{13}C NMR spectrum, δ, ppm: 28.32 ($2CH_2$, $^1J_{CH}$ 127 Hz), 40.94 ($2CH_2$, *cyclo*-Bu, $^1J_{CH}$ 138 Hz), 43.52 (2CHPh, $^1J_{CH}$ 139 Hz), 126.09 (2CH, Ph, $^1J_{CH}$ 159 Hz), 126.70 (4CH, Ph, $^1J_{CH}$ 156 Hz), 128.34 (4CH, Ph, $^1J_{CH}$ 161), 130.32 (CH=, $^1J_{CH}$ 168), 144.35 (2C, Ph), 150.34 (2C=). Mass spectrum MALDI-TOF: *m/z* 287 $[M+1]^+$.

1,1'-Ethane-1,2-diylbisspiro[3.5]non-1-ene (XXX). Yield 83%. ^{1}H NMR spectrum, δ, ppm: 1.11–1.54 m (20H), 2.03 br.s (4H, CH_2), 2.06 br.s (4H, CH_2), 5.65 br.s (2H, 2CH=). ^{13}C NMR spectrum, δ, ppm: 23.60 ($2CH_2$, $^1J_{CH}$ 127 Hz), 24.20 ($4CH_2$, $^1J_{CH}$ 126 Hz), 25.85 ($2CH_2$, $^1J_{CH}$ 124 Hz), 34.87 ($4CH_2$, $^1J_{CH}$ 124 Hz), 39.38 ($2CH_2$, *cyclo*-Bu, $^1J_{CH}$ 135 Hz), 49.17 (2C), 122.90 (2CH=, $^1J_{CH}$ 168 Hz), 159.03 (2C=). Mass spectrum, *m/z* (I_{rel}, %): 270 (12) $[M]^+$, 242 (8), 230 (12), 229 (100), 228 (27), 188 (11), 187 (17), 175 (12), 174 (57), 162 (10), 161 (57), 148 (22), 147 (21), 133 (18), 119 (25), 107 (36), 106 (26), 105 (30), 93 (92), 91 (68), 81 (57), 79 (74), 77 (38), 67 (65), 55 (36), 53 (11), 41 (34).

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