Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron 62 (2006) 8814–8821
Tetrahedron

Carbenoid rearrangement of *gem*-dihalogenospiropentanes

Elena B. Averina, Rashad R. Karimov, Kseniya N. Sedenkova, Yurii K. Grishin, Tamara S. Kuznetzova* and Nikolai S. Zefirov

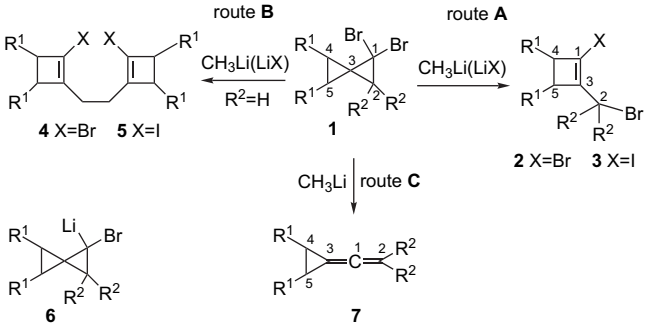
Department of chemistry, Moscow State University, Leninskie Gory, 119992 Moscow, Russian Federation

Received 17 April 2006; revised 7 June 2006; accepted 22 June 2006
Available online 21 July 2006

Abstract—A skeletal rearrangement of dihalogenospiropentanes in the presence of alkyllithium reagents has been systematically studied using a number of *gem*-dibromospiropentanes. The scope and limitations of this carbenoid rearrangement are outlined and its mechanism is discussed.

1. Introduction

In 1992 we reported the first example of the skeletal rearrangement of dibromospiranes of type **1** in the presence of MeLi.[1] The general pathways of this new rearrangement are shown in Scheme 1 (routes **A**, **B**). To the best of our knowledge, three short publications appeared afterward, where the products of the same rearrangement were documented.[2,3] The mechanism of this rearrangement was unclear and it was not discussed. The scope and limitations of this rearrangement remained unknown as well.



Scheme 1.

In principle, the reaction of dibromides **1** with MeLi proceeds to give the corresponding allenes **7** (route **C**, Scheme 1) as major products. However, lowering the reaction temperature up −55 °C leads to the rearrangement giving either cyclobutenes **2** (route **A**, Scheme 1) or compounds of type **4** (route **B**, Scheme 1) depending on the substituents in the cyclopropane ring. If starting methyllithium had been prepared from methyl iodide, the corresponding iodides **3** and/or **5** were also isolated. It was supposed that 'monomeric' rearranged products of types **2**, **3** are the intermediates in the formation of 'dimeric' products of types **4**, **5**.[1,2]

The main unusual feature of this rearrangement is to be emphasized: while the transformation **1**→**2** resembles rather *carbocationic* rearrangement (note also the formation of iodides **3**, **5** in the presence of LiI), the reaction conditions used suppose the intermediate formation of Li–C–Br carbenoid (**6**). Generally carbenoids have an *anionic* nature.[4,5] In other words, we deal with a formally cationic rearrangement in Li-carbenoid **6**, which undergoes nucleophilic attack during this process.

Being still not generally recognized, this controversial situation was nevertheless documented in the literature (e.g., "it was and still is indeed remarkable that… carbenoids (anions!) are electrophilic enough to react with rather weakly nucleophilic bonds"[5c]). Such electrophilic ability of different carbenoids has been evidently disclosed and carefully reviewed.[5] Especially noteworthy is that carbenoids of Li–C–Br type can react with such nucleophiles as C–H, C=C, and C–C bonds; the last reaction, which is still a rather rare case, represents the skeletal rearrangements in carbenoids.[5–8]

In this paper, we study the above mentioned carbenoid rearrangement systematically, using a number of substituted spiranes of type **1** to demonstrate the general character of this process, to trace the position of substituents in starting versus final materials, and to put forward some general conclusions about mechanism.

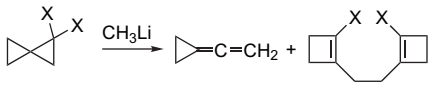
Keywords: *gem*-Dihalogenospiropentanes; Carbenoid rearrangement; Alkyllithium reagents; Bromocyclobutenes.
* Corresponding author. Tel.: +7 495 9393969; fax: +7 495 9390290; e-mail: kuzn@org.chem.msu.ru

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.06.086

2. Results

In previous works it was found[1,2] that lowering the temperature up to −55 °C favors the formation of the rearrangement products **2** or **4** (Scheme 1) and disfavors the formation of allenes **7** (route **C**, Scheme 1). Also, the reaction of dibromospiropentanes **1** with MeLi contaminated with LiI at elevated temperatures favors both the formation of allene **7** as well as *iodides* **3**, **5** and simultaneously the yields of the rearranged products decrease.[1] For example, we isolated the rearranged iodide **5** [R^1,R^2=H, R^1,R^1=–$(CH_2)_5$–] in the reaction of 10,10-dibromotricyclo-[7.1.0.$0^{1,3}$]decane [**1**, R^1,R^2=H, R^1,R^1=–$(CH_2)_5$–] at −5 °C in only 3% yield, the corresponding bicyclo[7.1.0]deca-1,2-diene being the major product (30% yield).[2]

Other reactions also proceeded accordingly (Scheme 1): the dibromide **8a** reacts with MeLi (LiI) at −55 °C to give allene **9** (10%), rearranged dimeric dibromide **10a** (64%), and rearranged diiodide **10b** (5%). Increasing the temperature of the same reaction up to 0–5 °C gave the same products but in the ratio **9**:**10a**:**10b**=30%:4%:17%. Thus, at higher temperatures the yields of dibromide **10a** were lowered and the yield of allene **9** and diiodide **10b** was increased substantially.



8a, X=Br
8b, X=I

9

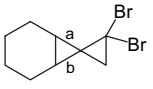
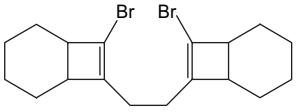
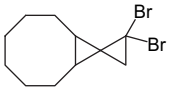
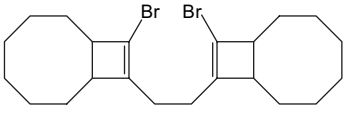
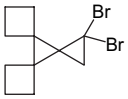
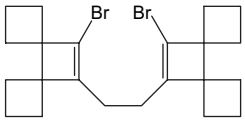
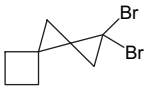
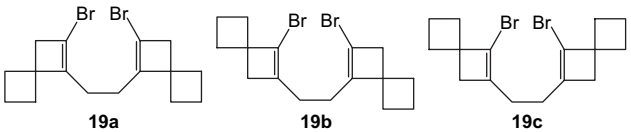
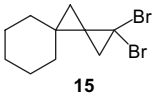
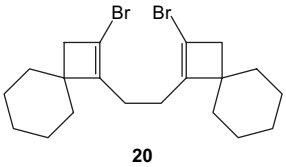
10a, X=Br
10b, X=I

It is of interest that a dramatic increase of the content of LiI in MeLi up to 5 equiv in the reaction run at −55 °C gave only unchanged starting dibromide **8a**. This result is in accordance with the data about lower reactivity of MeLi·LiI complex.[9] On the other hand, the reaction of diiodide **8b** with pure MeLi, not contaminated by LiI, gave rearranged diiodide **10b** in a good yield (45%).

Because the separation of bromides and iodides (in pairs **2/4** and **3/5**) is a difficult task, we used in this work the commercial MeLi, which was not contaminated with LiI or LiBr. All further reactions of dibromospiropentanes (**1**) were performed at −55 °C because at this temperature the ratio of corresponding allenes **7** to rearranged products (**2**, **4**) is minimal. The products composition in the reactions of some dibromides **1** with MeLi, *n*-BuLi, or *t*-BuLi was approximately the same. Allenes were not isolated as individual compounds but their yields were clearly determined by NMR spectroscopy. All products of rearrangement were isolated by preparative column chromatography and characterized by ^{1}H and ^{13}C NMR, mass spectra, and elemental analysis.

The results obtained with substituted dibromospiranes of type **1** (**11**–**15**) where R^2=H are summarized in Table 1. As expected, the reactions of **11**–**15** with MeLi proceeded to give mixtures of the corresponding allenes (10–25% yields) and the 'dimeric' products of rearrangement (**16**–**20**) (see Table 1). For dibromides **11**–**13**, having one symmetrically substituted cyclopropane ring (in a sense that

Table 1. Results of the reactions of dibromides **11**–**15** with MeLi

Starting dibromide	Products of rearrangement	Yield (%)
 **11**	 **16**	44
 **12**	 **17**	45
 **13**	 **18**	76
 **14**	 **19a** **19b** **19c**	50
 **15**	 **20**	75

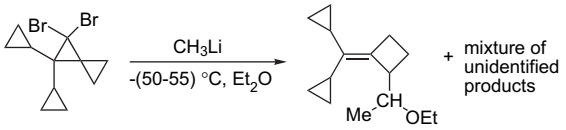
bond **a** is equivalent to bond **b**, see **11**), we isolated single rearranged products **16**–**18**, correspondingly. This is supported by the presence of signals of only two disubstituted C=C atoms in ^{13}C NMR at δ 109–117 and δ 143–155 ppm.

For dibromides **14** and **15** possessing non-equivalent bonds **a** and **b**, which may undergo migration one may expect the formation of three 'dimeric' compounds (two 'homodimeric' and one 'heterodimeric'). In principle, the most substituted bond has to be the most nucleophilic. Previously, we isolated the rearranged iodide **5** [R^1,R^2=H, R^1,R^1=–$(CH_2)_5$–] in the reaction of 10,10-dibromotricyclo[7.1.0.0^{1,3}]decane [**1**, R^1,R^2=H, R^1,R^1=–$(CH_2)_5$–], which supports migration of the monosubstituted bond.[2] However, the yield of the rearrangement product in this case is extremely small (3%) and this example cannot be generalized.

As can seen from Table 1, for the case of dibromide **14** we have observed exactly three rearranged products **19a**–**c**. Contrary to that for the case of dibromide **15** we isolated the single rearranged product **20** due to bond **a** migration. Thus, the data about the migration ability of bonds **a** versus **b** are still contradictory.

Next, dibromides of type **1**, which contain internal dibromospirane framework (**1**, where $R^2 \neq H$) (e.g., **21**) were studied. We have investigated first the tetracyclic dibromide **21** in the reaction with MeLi. The dibromide **21** contains two bonds, **a** and **b**, which presumably are able to migrate, being incorporated in spirosystem of type **1**. We have found that the rearrangement proceeds to give the only 'monomeric' product of type **2**: this is clear from the mass spectra of the obtained dibromide, which contained a triplet of molecular peak with *m*/*z* 332, 334, and 336. Moreover, the obtained product has definitely the structure of **22**, confirmed by its NMR spectra. The NMR spectrum of **22** has only one set of signals expected for one isomer from two possible. Two signals of CH-groups at δ 48.6 and δ 51.0 ppm are observed and they confirm the presence of the 3,4-disubstituted cyclobutene fragment. The value of coupling constants $^1J_{CH}$ of CH-group of cyclobutene fragment is assigned to coupling constants for four-membered ring ($^1J_{CH}$ 141 and 139 Hz).[10] Two signals of CH_2-groups at δ 13.8 and δ 17.4 ppm have large C–H coupling constants ($^1J_{CH}$ 165 and 164 Hz), which are typical for cyclopropanes and can be assigned to a 1,1-disubstituted cyclopropane fragment.[10] Thus, this rearrangement proceeds with the migration of the bond **a** of the substituted three-membered ring to give rearrangement dibromide **22**.

Then, we investigated the tetracyclic dibromide **24** in the reaction with MeLi. The dibromide **24** contains unsubstituted cyclopropane rings incorporated in the spirosystem of type **1**, which was shown to be inert in the case of dibromide **24**. This reaction gave a complex mixture of products; the major of them was identified as the ether **25**, which was formed due to capture of solvent molecule by some carbene (carbenoid) intermediate. Compound **25** is rather unstable and can be characterized only by spectroscopy.



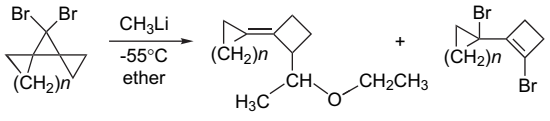
24 **25**

In order to clarify the formation of ether **25**, we note that carbenes, including the cyclopropylidene, can form the products of intermolecular insertion into α-C–H-bond of the solvent, i.e., ether.[11–13] Thus, isolation of the ether **25** might indicate the transient formation of the corresponding methylenecyclobutylidene in the process (vide infra), which is able to react with the diethyl ether solvent.

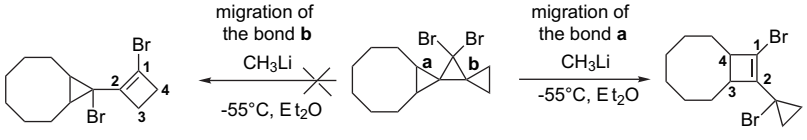
The behavior of tricyclic dibromide **26a** was also investigated in this rearrangement. By analogy with dibromide **24** one may expect either the formation of the ether **27a** or rearranged dibromide type **2**. However, the previous literature data have shown that the treatment of dibromide **26a** by MeLi or *t*-BuLi (−45 °C) provided a mixture of eight different products with the formation of ether **27a** as the major one (up to 40%).[13] In this reaction bromo containing compounds were obtained; however, they are not the product of dibromospiropentane rearrangement or related compounds, which could have been obtained by its dehydrobromination.

Thus, we decided to reinvestigate the reaction of dibromide **26a** with MeLi at −55 °C. The product **27a** was obtained in a high yield (89%) under these conditions. To our surprise, we did not observe other products in this reaction.

We should mention here also that this result is in contrast with behavior of dibromide **26b**, which did indeed give the rearranged dibromide **27b** in high yield (77%).[1,14]



26a *n*=4
26b *n*=1 **27a** *n*=4 **27b** *n*=1

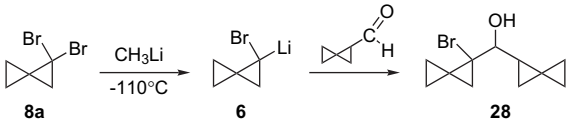


23 **21** **22**, *70%*

3. Discussion

The first conclusion, which can be derived from the results obtained, that this rearrangement under investigation, which was observed by us previously only for a few cases,[1,2] has in fact the general character, and it was established now for a variety of *gem*-dihalogenated spirocyclopropanes of type **1**. This is remarkable because there are many publications concerning the reactions of dibromides of type **1** with Alk-Li, where the rearranged products were not observed.[1b,15] This may be explained either by inconvenient conditions for the rearrangement or by loss of the minor rearranged product/s during purification.

The mechanistic rationalization of the whole process can be presented as follows (Scheme 2). For clarity we will use pure carbocationic stepwise presentation, thus, ignoring the problem of concerted mechanistic steps. First step of the reaction of dibromides of type **1** with MeLi seems to lead to the formation of lithium carbenoid of type **6** via halogenophilic attack. While this step is well documented in literature,[11,12,16] we decided to prove unambiguously the intermediate of Li-carbenoid **6** as well as its anionic character. We have found that the addition of cyclopropyl aldehyde to the intermediate **6** (R=R^1=H) leads to its trapping with the formation of alcohol **28**.[17]



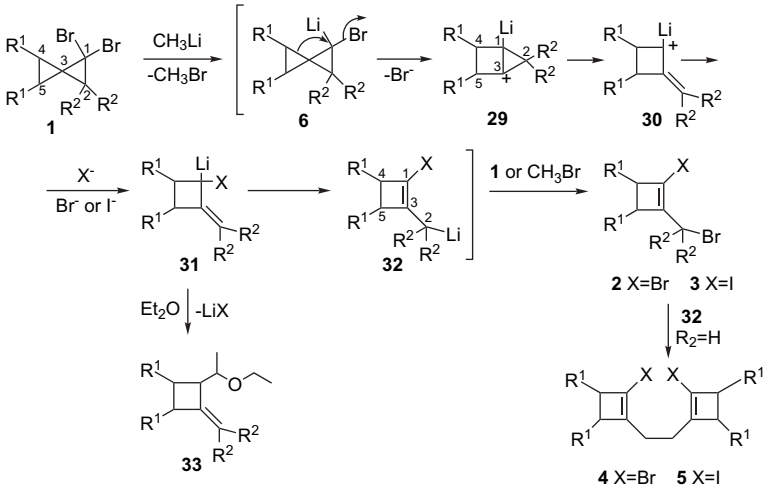
Next logical step is the manifestation of electrophilic nature of intermediate carbenoid **6**, which means principle acceptance of nucleophilic attack on carbenoid center.[5]

It means that we assume the second step of the whole process as **6**→**29**, in which the C–C bond of second three-membered ring (being enough nucleophilic as compared with normal C–C bonds) acts as a nucleophile leading to an S_N2-like displacement of the leaving group –Br from the electrophilic carbenoid carbon atom to give cation **29**. The driving forces for this step could be release of cyclopropane strain.

Geometry of this cation is not very favorable and it subsequently rearranges into cation **30**. It is to be noted that analogous pure carbocationic rearrangement during the deamination of aminospiro[2.2]pentane with intermediacy of unsubstituted cations of types **29** and **30** was observed.[18] However, the introduction of structure **30** is feasible but still risky.[18,19] Lithium being extremely electron donor substituent should stabilize the carbocationic center, but we do not know any theoretical calculations or experimental evidences for such type of Li-substituted cations. On the other hand, the acceptance of intermediate cation **30** permits to explain competitive participation of such external nucleophile as I^- in the next step of the reaction, **30**→**31**. Indeed, this step leads to the formation of a new carbenoid **31**, where X=Br or I.

Depending on the structure, this carbenoid **31** plays role as an intermediate for two ramificated pathways (Scheme 2). One of them is the insertion reaction into C–H bond of the ether used as solvent, which gives the compounds of type **33** (above mentioned **25**, **27a**). This insertion probably proceeds via formation of the corresponding carbene, namely substituted methylenecyclobutylidene. As it was mentioned above, it is well known that carbenes demonstrate the ability to insertion reactions into C–H and C–C bonds.[20] Also, it is known that cyclopropylidene, which is obtained from dibromocyclopropanes under treatment with alkyllithium reagents under temperatures above −80 °C, exhibits also the insertion into C–H and C–C bonds.[11,12]

Second route of the transformation of carbenoid **31** leads to 'dimeric' products of types **4** and **5**. One feasible explanation can be the following. This route includes several steps, the first being the following. The carbenoid **31**, which is lithium allylic derivative, may be prone to [1,3]-sigmatropic migration of C–Li bond to give the lithium derivative **32**. The sigmatropic tautomerism of allyllithium derivatives (or even acceptance of pure ionic structure) is well documented in literature (see for example Ref. 21). In turn, Li-derivative **32** can compete with starting MeLi in halogenophilic attack on dibromide **1** to give the carbenoid **6** and bromide **2** (or **3**; Scheme 2).

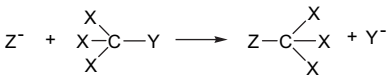


Scheme 2.

Further transformations of bromide **2** or **3** (Scheme 2) crucially depend on the nature of substituents R^2. In the case of $R^2 \neq H$ the *tert*-C–Br fragment is non-reactive may be due to steric reasons and the bromide/s can be isolated. In contrast, if R^2=H, the primary C–Br reacts with Li-derivative **32** to give coupling 'dimeric' products **4** or **5**. An example of this route in X-philic reactions has been illustrated in literature.[22,23]

Thus, the suggested mechanistic rationalization of the discovered rearrangement permits to explain the whole course of this process. The principle point of suggested scheme is the acceptance of carbocationic pathways in Li-carbenoid intermediates.

Some points discussed above may have more general value and can be generalized to be a guideline for future studies. Why the concept of ability of carbenoids of type Li–C–Br (*anions*: Li–C–Br↔Li^+ $^-$C–Br) to undergo *nucleophilic* attack, having been clearly documented by experiments, still has not acquired general understanding? Because these facts were not treated by a general theory of nucleophilic substitution. Indeed, while there exist endless numbers of publications concerning the detailed theoretical description of the process of nucleophilic substitution (Eq. 1), one point (to the best of our knowledge) is not clear enough: namely, the *influence of X-substituents on this process for the whole range of possibilities*.



(1)

Two opposite limiting cases can be roughly outlined. The increasing of X-electronegativities should lead to a decrease in the rate of S_N2-substitution and, in extreme case, has to change the reactivity mode to SET or X-philic pathway.[22–24]

In turn, the decrease in X-electrophilicities should lead to the increase in the rate of S_N2-substitution. Strong stabilization may lead also to a change of mode reactivity (e.g., from S_N2 to S_N1 pathway). The questions may be posed: which mode will be the case with X=Li or MgX, or another related extreme donor? Which kind of new reactivity pathway can be detected?

In this connection the structure of Li-carbenoid **6**, may be considered as an example of such limiting case. In summary the theoretical investigation of the process of Eq. 1 for the whole range of X-electronegativities including limiting cases may be useful in understanding where and why one can expect existence of unusual pathways, leading to unusual reactions.

4. Experimental

4.1. General

NMR spectra were recorded on a 'Bruker DPX-400' spectrometer (400.13 and 100.62 MHz, for ^1H and ^{13}C, respectively) at room temperature; the chemical shifts δ were measured in parts per million with respect to solvent (^1H: $CDCl_3$, δ=7.24 ppm; ^{13}C: $CDCl_3$, δ=77.13 ppm). Mass spectra were taken on Finnigan MAT 95 XL (70 eV) using electron impact ionization (EI) and GC–MS coupling. Microanalyses were performed on a Karlo Erba 1106 instrument. Analytical thin-layer chromatography (TLC) was carried out with Silufol silica gel plates (supported on aluminum); the revelation was done by UV lamp (254 and 365 nm) and chemical staining (iodine vapor). Melting points (mp) were determined on a Electrothermal 9100 capillary apparatus and are uncorrected. Column chromatography was performed using silica gel 60 (230–400 mesh, Merck). Petroleum ether (PE) used refers to the 40–60 °C boiling point fraction. All reagents, except commercial products of satisfactory quality were purified with literature procedures prior to use. Starting compounds: methylenecyclopropane,[25] 1-methylenespiro[2.3]hexane,[26] 1-methylenespiro[2.5]octane,[27] 9-methylenedispiro[3.0.3.1]nonane,[28] 7-methylenebicyclo[4.1.0]heptane,[29] 9-methylenebicyclo-[6.1.0]nonane,[29] 9-cyclopropylidenebicyclo[6.1.0]nonane,[30] cyclopropylidenecyclohexane,[31] 1,1′,1″-methanediylylidenetricyclopropane,[32] and 1,1-dibromospiro[2.2]pentane (**8a**)[33] were synthesized by known procedures.

4.1.1. 1,1-Diiodospiro[2.2]pentane (8b).[34] To a stirred solution of *t*-BuOK (3.2 g, 28 mmol) and olefin (5.4 g, 7.5 mL, 100 mmol) in *t*-BuOH (30 mL) at −30 °C under argon, iodoform (10.0 g, 25 mmol) was added. After 1 h the resulting mixture was allowed to −(5–10) °C and then, after 6 h, quenched with cold water (50 mL). The aqueous layer was extracted with petroleum ether (3×20 mL) and combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product were purified by column chromatography (silica gel, petroleum ether). Yield: 4.42 g (55%), yellow oil, R_f=0.75 (petroleum ether). ^1H NMR: δ 1.01–1.07 (m, 2H), 1.42–1.49 (m, 2H), 2.22 (s, 2H). ^{13}C NMR: δ −55.8 (CI_2), 16.3 (J=169, 2×CH_2), 22.0 (C), 32.2 (J=167, CH_2). MS (EI, 70 eV) *m*/*z* (rel. int., %): 320 (9) $[M]^+$, 193 (53) $[M-I]^+$, 165 (14), 127 (7), 66 (100).

4.2. General procedure 1. Preparation of the substituted *gem*-dibromospiropentanes 11–15, 21, 24, 26a, 26b

To a stirred mixture of *t*-BuOK (4.3 g, 38 mmol) and olefin (19 mmol) in petroleum ether (15 mL) at 0 °C under argon, a solution of bromoform (5.82 g, 2 mL, 23 mmol) in petroleum ether (5 mL) was added dropwise. After 20 min the resulting mixture was slowly allowed to warm to room temperature and then, after 4–48 h, quenched with cold water (40 mL). The aqueous layer was extracted with Et_2O (3×20 mL) and combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude dibromides were purified by distillation.

4.2.1. 2′,2′-Dibromospiro[bicyclo[4.1.0]heptane-7,1′-cyclopropane] (11). Reaction mixture was stirred for 4 h. Yield: 2.71 g (51%), white solid, mp 49 °C, bp 62–65 °C/2 mmHg. ^1H NMR: δ 1.10–1.38 (m, 4H), 1.39–1.52 (m, 2H), 1.58–1.63 (m, 2H), 1.81 (s, 2H, cy-Pr), 1.81–1.95 (m, 2H). ^{13}C NMR: δ 21.0 (2×CH, cy-Pr), 21.3 (2×CH_2, cy-Hex), 21.7 (2×CH_2, cy-Hex), 26.2 (CH_2, cy-Pr), 32.3

(C), 35.6 (CBr_2). Anal. Calcd for $C_9H_{12}Br_2$: C, 38.61; H, 4.32%. Found: C, 38.56; H, 4.00%.

4.2.2. 2′,2′-Dibromospiro[bicyclo[6.1.0]nonane-9,1′-cyclopropane] (12). Reaction mixture was stirred for 6 h. Yield: 3.75 g (64%), white solid, mp 61.5 °C, bp 95–98 °C/2 mmHg. ^{1}H NMR: δ 1.01–1.19 (m, 2H, 2×CH, cy-Pr), 1.39–1.56 (m, 6H), 1.58–1.69 (m, 2H), 1.70–1.78 (m, 2H), 1.75 (s, 2H, cy-Pr), 1.79–1.89 (m, 2H). ^{13}C NMR: δ 24.7 (2×CH_2, cy-Oct), 25.2 (2×CH, cy-Pr), 26.5 (2×CH_2, cy-Oct), 26.7 (2×CH_2, cy-Oct), 28.7 (CH_2, cy-Pr), 30.6 (C), 35.8 (CBr_2). Anal. Calcd for $C_{11}H_{16}Br_2$: C, 42.89; H, 5.24%. Found: C, 42.66; H, 5.50%.

4.2.3. 1,1-Dibromotrispiro[2.0.3^4.0.3^8.0^3]undecane (13). Reaction mixture was stirred for 6 h. Yield: 3.66 g (63%), colorless liquid, bp 85 °C/2 mmHg. ^{1}H NMR: δ 1.79 (s, 2H, cy-Pr), 1.80–1.89 (m, 2H), 1.92–2.16 (m, 8H), 2.50–2.62 (m, 2H). ^{13}C NMR: δ 16.2 (J=138, 2×CH_2, cy-Bu), 21.9 (J=141, 2×CH_2, cy-Bu), 25.3 (J=141, 2×CH_2, cy-Bu), 27.2 (J=166, CH_2, cy-Pr), 31.9 (2×C), 36.0 (C), 36.4 (C). Anal. Calcd for $C_{11}H_{14}Br_2$: C, 43.17; H, 4.61%. Found: C, 43.07; H, 4.68%.

4.2.4. 1,1-Dibromodispiro[2.0.3.1]octane (14). Reaction mixture was stirred for 4 h. Yield: 4.19 g (83%), colorless liquid, bp 55–56 °C/2 mmHg. ^{1}H NMR: δ 1.05 (d, ^2J=5.2, 1H, cy-Pr), 1.15 (d, ^2J=5.2, 1H, cy-Pr), 1.83 (d, ^2J=6.2, 1H, cy-Pr), 1.98 (d, ^2J=6.2, 1H, cy-Pr), 1.88–2.24 (m, 5H), 2.71–2.82 (m, 1H). ^{13}C NMR: δ 17.0 (J=136, CH_2, cy-Bu), 21.7 (J=162, CH_2, cy-Pr), 25.8 (J=136, CH_2, cy-Bu), 28.3 (J=166, CH_2, cy-Pr), 29.3 (J=137, CH_2, cy-Bu), 31.3 (C), 33.1 (C), 33.4 (C). Anal. Calcd for $C_8H_{10}Br_2$: C, 36.13; H, 3.79%. Found: C, 36.46; H, 3.90%.

4.2.5. 1,1-Dibromodispiro[2.0.5.1]decane (15). Reaction mixture was stirred for 6 h. Yield: 2.90 g (52%), colorless liquid, bp 92–93 °C/2 mmHg. ^{1}H NMR: δ 0.84 (d, ^2J=4.5, 1H, cy-Pr), 0.95 (d, ^2J=4.5, 1H, cy-Pr), 1.15–1.41 (m, 2H), 1.42–1.66 (m, 6H), 1.74–1.88 (m, 2H), 1.79 (d, ^2J=6.2, 1H, cy-Pr), 1.92 (dd, ^2J=6.2, ^4J=0.8, 1H, cy-Pr). ^{13}C NMR: δ 22.8 (J=164, CH_2, cy-Pr), 25.3 (CH_2), 25.7 (CH_2), 26.0 (CH_2), 27.7 (J=165, CH_2, cy-Pr), 30.4 (C), 32.2 (C), 32.3 (CH_2), 34.0 (CH_2), 36.2 (CBr_2). Anal. Calcd for $C_{10}H_{14}Br_2$: C, 40.85; H, 4.80%. Found: C, 40.87; H, 4.75%.

4.2.6. 3′,3′-Dibromodispiro[bicyclo[6.1.0]nonane-9,1′-cyclopropane-2′,1″-cyclopropane] (21).[34] Reaction mixture was stirred for 16 h. Yield: 0.44 g (44%), colorless oil, R_f=0.6 (petroleum ether). ^{1}H NMR: δ 0.77–0.91 (m, 4H), 1.05–1.79 (m, 12H), 1.80–1.89 (m, 2H). ^{13}C NMR: 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 (rel. int., %): 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).

4.2.7. 1,1-Dibromo-2,2-dicyclopropylspiro[2.2]pentane (24).[35] Reaction mixture was stirred for 24 h. Yield: 2.67 g (46%), colorless liquid, bp 92–95 °C/2 mmHg. ^{1}H NMR: δ 0.18–0.26 (m, 2H), 0.41–0.49 (m, 2H), 0.52–0.68 (m, 4H), 0.91–0.99 (m, 2H), 1.01 (br s, 4H). ^{13}C NMR: δ 2.9 (J=161, 2×CH_2), 3.6 (J=161, 2×CH_2), 10.0 (J=165, 2×CH_2), 15.8 (J=160, 2×CH), 31.7 (C), 35.8 (C), 49.1 (CBr_2). Anal. Calcd for $C_{11}H_{14}Br_2$: C, 43.17; H, 4.61%. Found: C, 43.21; H, 4.57%.

4.2.8. 10,10-Dibromodispiro[2.0.5.1]decane (26a).[13] Reaction mixture was stirred for 48 h. Yield: 4.24 g (76%), white solid, mp 50 °C, R_f=0.8 (petroleum ether). ^{1}H NMR: 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: 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 $C_{10}H_{14}Br_2$: C, 40.85; H, 4.80%. Found: C, 40.59; H, 5.01%.

4.2.9. 7,7-Dibromodispiro[2.0.2.1]heptane (26b).[33] Reaction mixture was stirred for 5 h. Yield: 2.92 g (61%), white solid, mp 71 °C, bp 75–76 °C/8 mmHg. ^{1}H NMR: δ 1.07–1.13 (m, 4H), 1.23–1.29 (m, 4H). ^{13}C NMR: δ 11.2 (4×CH_2), 31.9 (C), 40.7 (CBr_2).

4.3. General procedure 2. Reaction of the substituted *gem*-dihalogenospiropentanes 8a, 8b, 11–15, 21, 24, 26a, 26b with alkyllithium

To a stirred solution of *gem*-dihalogenospiropentanes (3.3 mmol) in Et_2O (10 mL) at −(55–60) °C under argon, methyllithium (solution in Et_2O, 2.75 mL, 1.6 M, 4.4 mmol) was added dropwise for 45 min. After 1 h the resulting mixture was slowly allowed to 0 °C and then quenched with cold water (20 mL). The aqueous layer was extracted with Et_2O (3×10 mL) and combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude products were purified by column chromatography (silica gel, petroleum ether).

The reaction of 1,1-dibromospiro[2.2]pentane (**8a**) (0.75 g, 3.3 mmol) with butyllithium (solution in hexane, 2.75 mL, 1.6 M, 4.4 mmol) or *tert*-butyllithium (solution in pentane, 2.93 mL, 1.5 M, 4.4 mmol) proceeds according to the method described above.

4.3.1. 1,1′-Ethane-1,2-diylbis(2-bromocyclobutene) (10a).[1a] Yield in reaction **8a** with methyllithium: 0.29 g (60%); yield in reaction **8a** with butyllithium: 0.28 g (58%); yield in reaction **8a** with *tert*-butyllithium: 0.16 g (34%); colorless oil, R_f=0.8 (petroleum ether). ^{1}H and ^{13}C NMR data for the **10a** are the same as those reported in literature.[1a]

4.3.2. 1,1′-Ethane-1,2-diylbis(2-iodocyclobutene) (10b).[34] Yield: 0.29 g (45%), colorless oil, R_f=0.6 (petroleum ether). ^{1}H NMR: δ 2.09 (s, 4H), 2.70 (s, 8H). ^{13}C NMR: δ 27.5 (J=129, 2×CH_2), 34.4 (J=142, 2×CH_2), 36.4 (J=143, 2×CH_2), 83.5 (CI_2), 156.1 (C). MS (EI, 70 eV) m/z (rel. int., %): 386 (21) [M]$^+$, 259 (45) [M−I]$^+$, 231 (8), 245 (81), 132 (94), 131 (100), 117 (68), 91 (55), 77 (20), 65 (9), 51 (8), 39 (7).

4.3.3. 7,7′-Ethane-1,2-diylbis(8-bromobicyclo[4.2.0]oct-7-ene) (16). Yield: 0.29 g (44%), colorless oil, R_f=0.6 (petroleum ether). ^{1}H NMR: δ 1.31–1.75 (m, 16H), 2.05–2.39 (m, 4H), 2.83–3.05 (m, 4H). ^{13}C NMR: δ 17.7 (2×CH_2), 18.1 (CH_2), 18.2 (CH_2), 22.5 (2×CH_2), 23.2 (CH_2),

23.2 (CH_2), 24.1 (CH_2), 24.3 (CH_2), 40.8 (CH), 41.1 (CH), 45.5 (2×CH), 113.5 (C), 113.6 (C), 149.7 (C), 149.9 (C). Anal. Calcd for $C_{18}H_{24}Br_2$: C, 54.02; H, 6.04%. Found: C, 54.05; H, 6.04%.

4.3.4. 9,9′-Ethane-1,2-diylbis(10-bromobicyclo[6.2.0]-dec-9-ene) (17). Yield: 0.34 g (45%), colorless oil, R_f=0.6 (petroleum ether). ^{1}H NMR: δ 1.22–1.48 (m, 16H), 1.53–1.79 (m, 8H), 2.03–2.25 (m, 4H), 2.65–2.73 (m, 2H), 2.75–2.82 (m, 2H). ^{13}C NMR: δ 23.1 (CH_2), 23.4 (CH_2), 25.2 (4×CH_2), 25.9 (2×CH_2), 26.3 (2×CH_2), 29.6 (2×CH_2), 29.9 (2×CH_2), 47.4 (CH), 47.8 (CH), 52.2 (2×CH), 114.3 (C), 114.5 (C), 148.2 (C), 148.4 (C). Anal. Calcd for $C_{22}H_{32}Br_2$: C, 57.91; H, 7.07%. Found: C, 57.79; H, 7.21%.

4.3.5. 9,9′-Ethane-1,2-diylbis(10-bromodispiro[3.0.3.2]-dec-9-ene) (18). Yield: 0.57 g (76%), colorless oil, R_f=0.4 (petroleum ether). ^{1}H NMR: δ 1.63–1.91 (m, 8H), 1.98–2.17 (m, 16H), 2.37 (s, 4H). ^{13}C NMR: δ 15.0 (J=135, 2×CH_2), 15.8 (J=135, 2×CH_2), 23.4 (J=130, 2×CH_2), 27.1 (J=134, 4×CH_2), 28.4 (J=135, 4×CH_2), 55.9 (C), 59.8 (C), 118.3 (C), 149.1 (C). Anal. Calcd for $C_{22}H_{28}Br_2$: C, 58.42; H, 6.24%. Found: C, 58.72; H, 6.44%.

4.3.6. 1,1′-Ethane-1,2-diylbis(2-bromospiro[3.3]hept-1-ene) (19a), 2-bromo-1-[2-(1-bromospiro[3.3]hept-1-en-2-yl)ethyl]spiro[3.3]hept-1-ene (19b), and 2,2′-ethane-1,2-diylbis(1-bromospiro[3.3]hept-1-ene) (19c). Yield for the mixture of three isomers (A:B:C=4:2:1): 0.31 g (50%), colorless oil, R_f=0.7 (petroleum ether). ^{1}H NMR (for mixture of three isomers): δ 1.71–1.96 (m, 4H+4H+4H), 2.01–2.34 (m, 8H+8H+8H), 2.37 (br s, 4H, A), 2.49 (br s, 4H, C), 2.54 (br s, 4H, B), 2.73 (br s, 4H, B), 2.76 (br s, 4H, A), 2.82 (br s, 4H, C). ^{13}C NMR (for mixture of three isomers): δ 15.7 (2×CH_2), 16.27 (2×CH_2), 16.30 (2×CH_2), 23.5 (2×CH_2+2×CH_2), 25.1 (2×CH_2), 29.3 (2×CH_2+2×CH_2), 29.7 (2×CH_2), 30.75 (2×CH_2+2×CH_2), 30.80 (2×CH_2), 44.0 (C), 44.3 (C), 45.0 (C), 50.5 (2×CH_2+2×CH_2), 51.5 (2×CH_2), 109.3 (C), 109.5 (C), 117.2 (C), 143.7, 151.3 (C), 151.5 (C). MS (EI, 70 eV) m/z (rel. int., %): 374 (0.2), 372 (0.6), 370 (0.2) $[M]^+$, 293 (5), 291 (5) $[M-Br]^+$, 211 (24), 183 (27), 155 (38), 141 (38), 128 (40), 115 (38), 105 (56), 91 (100), 77 (58), 65 (27), 53 (22), 39 (27). Anal. Calcd for $C_{16}H_{20}Br_2$: C, 51.64; H, 5.42%. Found: C, 51.47; H, 5.69%.

4.3.7. 1,1′-Ethane-1,2-diylbis(2-bromospiro[3.5]non-1-ene) (20). Yield: 0.53 g (75%), colorless oil, R_f=0.6 (petroleum ether). ^{1}H NMR: δ 1.09–1.24 (m, 2H), 1.25–1.41 (m, 4H), 1.48–1.74 (m, 14H), 2.23 (s, 4H), 2.47 (s, 4H). ^{13}C NMR 23.4 (J=130, 2×CH_2), 24.4 (J=123, 4×CH_2), 25.5 (J=119, 2×CH_2), 34.4 (J=124, 4×CH_2), 48.0 (J=141, 2×CH_2), 50.4 (2C), 109.4 (C), 155.3 (C). Anal. Calcd for $C_{20}H_{28}Br_2$: C, 56.09; H, 6.59%. Found: C, 56.00; H, 6.27%.

4.3.8. 9-Bromo-10-(1-bromocyclopropyl)bicyclo[6.2.0]-dec-9-ene (22).[34] Yield: 0.31 g (70%), colorless oil, R_f=0.6 (petroleum ether). ^{1}H NMR: 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: δ 13.9 (J=165, CH_2, cy-Pr), 17.4 (J=164, CH_2, cy-Pr), 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, CH, cy-Bu), 51.1 (J=139, CH, cy-Bu), 114.5 (C), 147.3 (C). MS (EI, 70 eV) m/z (rel. int., %): 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).

4.3.9. 1-[2-(Dicyclopropylmethylene)cyclobutyl]ethyl ethyl ether (25).[34] Yield: 0.42 g (58%), colorless oil. ^{1}H NMR (for fragment cy-Bu-CH(CH_3)OEt): δ 1.12 (t, ^3J=7.1, 3H, CH_3), 1.12 (d, ^3J=6.3, 3H, CH_3), 2.79–2.86 (m, 1H, CH, cy-Bu), 3.44 (q, ^3J=7.1, 2H, CH_2O), 3.70 (dq, ^3J=6.3, ^3J=6.3, 1H, CHO). ^{13}C NMR: δ 3.2 (CH_2), 3.5 (CH_2), 4.5 (CH_2), 5.0 (CH_2), 10.5 (CH), 12.3 (CH), 15.6 (2×CH_3), 17.9 (CH_2), 28.9 (CH_2), 47.0 (CH), 63.9 (CH_2), 76.0 (CH), 125.4 (C), 131.0 (C). MS (EI, 70 eV) m/z (rel. int., %): 220 (15) $[M]^+$, 147 (58) $[M-(CH_3)CHOEt)]^+$, 121 (23), 105 (23), 91 (26), 73 (100), 67 (11), 45 (58).

4.3.10. [2-(1-Ethoxyethyl)cyclobutylidene]cyclohexane (27a).[13] Yield: 0.61 g (89%), colorless oil, R_f=0.7 (petroleum ether). ^{1}H NMR: δ 1.15 (dd, ^3J=6.8, ^3J=6.3, 3H, CH_3), 1.19 (d, ^3J=5.5, 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), 3.39–3.53 (m, 2H, CH_2O), 3.53–3.61 (m, 1H, CHO). ^{13}C NMR: δ 15.7 (J=126, CH_3), 15.9 (J=126, CH_3), 17.8 (J=136, CH_2), 26.6 (CH_2), 26.8 (CH_2), 27.6 (CH_2), 27.7 (CH_2), 29.2 (CH_2), 29.7 (CH_2), 46.3 (J=134, CH), 63.9 (J=140, CH_2O), 76.6 (J=139, CH), 129.4 (C), 131.9 (C). MS (EI, 70 eV) m/z (rel. int., %): 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).

4.3.11. 1-Bromo-2-(1-bromocyclopropyl)cyclobutene (27b).[1a] Yield: 0.66 g (77%), colorless liquid, R_f=0.35 (petroleum ether). ^{1}H and ^{13}C NMR data for the **27b** are the same as those reported in literature.[1a]

4.3.12. (1-Bromospiro[2.2]pent-1-yl)(spiro[2.2]pent-1-yl)methanol (28). To a stirred solution of *gem*-dibromospiropentane **8a** (0.96 g, 3.3 mmol) in THF (30 mL) and pentane (10 mL) at −100 °C under argon, butyllithium (2.2 mL, 1.5 N, 3.3 mmol) was added dropwise for 15 min. The mixture was stirring at the same temperature for 1 h and then at −(110–115) °C spiro[2.2]pentane-1-carbaldehyde (0.32 g, 3.3 mmol) was added for 10 min. After 3 h the resulting mixture was quenched with cold 0.1 N H_2SO_4 (50 mL). The aqueous layer was extracted with Et_2O (3×10 mL) and combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude products were purified by column chromatography (silica gel, petroleum ether). Yield: 0.38 g (47%), colorless oil, n_D^{20}=1.5140. ^{1}H NMR (mixture of four isomers): δ 0.65–1.70 (m, 4×13H), 2.82 (d, ^3J=7.8, 1H, C*H*OH), 2.94 (d, ^3J=7.4, 1H, C*H*OH), 3.13 (d, ^3J=7.1, 1H, C*H*OH), 3.44 (d, ^3J=3.4, 1H, C*H*OH). Anal. Calcd for $C_{11}H_{15}BrO$: C, 54.34; H, 6.22%. Found: C, 54.67; H, 6.58%.

Acknowledgements

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

References and notes

1. (a) Lukin, K. A.; Zefirov, N. S.; Yufit, D. S.; Struchkov, Yu. T. *Tetrahedron* **1992**, *48*, 9977–9984; (b) Lukin, K. A.; Zefirov, N. S. Spiroannulated Cyclopropanes. In *Chemistry of Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, UK, 1995; pp 861–885.
2. (a) Averina, E. B.; Kuznetsova, T. S.; Zefirov, A. N.; Koposov, A. E.; Grishin, Yu. K.; Zefirov, N. S. *Mendeleev Commun.* **1999**, 101–102; (b) Averina, E. B.; Kuznetsova, T. S.; Lysov, A. E.; Potekhin, K. A.; Zefirov, N. S. *Dokl. Acad. Nauk* **2000**, *375*, 481–483 (Russ.); *Dokl. Chem.* **2000**, *375*, 257–259 (Engl. Transl.).
3. Borer, M.; Neuenschwander, M. *Helv. Chim. Acta* **1997**, *80*, 2486–2501.
4. Seyferth, D.; Welsch, D. E.; Raab, G. *J. Am. Chem. Soc.* **1962**, *84*, 4266–4269.
5. (a) Kobrich, G.; Akhtar, A.; Ansari, F.; Breckoff, W. E.; Buttner, H.; Drischel, W.; Fischer, R. H.; Flory, K.; Frohlich, H.; Goyert, W.; Heinemann, H.; Hornke, I.; Merkle, H. R.; Trapp, H.; Zundorf, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *79*, 15–27; (b) Warner, P. M.; Chang, S.-C.; Koszewski, N. J. *J. Org. Chem.* **1985**, *50*, 2605–2606; (c) Boche, G.; Lohrenz, C. W. *Chem. Rev.* **2001**, *101*, 697–756.
6. Bothner-By, A. A. *J. Am. Chem. Soc.* **1955**, *77*, 3293–3296.
7. Kirmse, W.; Wachtershauser, G. *Tetrahedron* **1966**, *22*, 73–80.
8. Skattebol, L. *Tetrahedron* **1967**, *23*, 1107–1117.
9. Talalaeva, T. V.; Rodionov, A. N.; Kocheshkov, K. A. *Dokl. Acad. Nauk SSSR* **1961**, *140*, 847–850 (Russ.); *Chem. Abstr.* **1962**, *56*, 5989f.
10. Kalinovsky, H. O.; Berger, S.; Brown, S. *^{13}C-NMR-Spektroskopie*; Georg Thieme: Stuttgart, 1984; pp 424–461.
11. Bolesov, I. G.; Kostikov, R. R.; Baird, M. S.; Tverezovsky, V. V. Synthetically Useful Transformations of Cyclopropylidenes Derived from Dihalocyclopropanes. In *Modern Problems of Organic Chemistry*; Potekhin, A. A., Kostikov, R. R., Eds.; St. Petersburg University Press: St. Petersburg, 2001; pp 76–112.
12. Backes, J.; Brinker, U. H. Cyclopropylidene. In *Houber–Weyl*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E 19b, pp 391–510.
13. Bertrand, M.; Tubul, M.; Ghiglion, C. *J. Chem. Res., Miniprint* **1983**, 2273–2281.
14. We reinvestigated the reaction of **26b** with methyllithium and established that only compound **27b** formed in this reaction.
15. (a) Fitjer, L.; Conia, J.-M. *Angew. Chem., Int. Ed. Engl.* **1973**, *85*, 832–833; (b) Lukin, K. A.; Kozhushkov, S. I.; Andrievsky, A. A.; Ugrak, B. I.; Zefirov, N. S. *J. Org. Chem.* **1991**, *56*, 6176–6179.
16. Braun, M. Lithium Carbenoid. In *The Chemistry of Organolithium Compounds*; Rappoport, Z., Ed.; Wiley: Chichester, UK, 2004; pp 829–900.
17. This experiment was made in collaboration with A. A. Adreevsky. Andreevsky, A. A. Diploma thesis, Moscow State University, 1992 (unpublished).
18. Applequist, D. E.; Johnston, M. R.; Fisher, F. *J. Am. Chem. Soc.* **1970**, *92*, 4614–4617.
19. Gajewski, J. J.; Chang, M. J. *J. Org. Chem.* **1978**, *43*, 765–767.
20. Kirmse, W. *Carbene Chemistry*; Academic: New York, NY, 1971.
21. (a) West, P.; Purmort, J. I.; McKinley, S. V. *J. Am. Chem. Soc.* **1968**, *90*, 797–798; (b) Jonson, C. S., Jr.; Weiner, M. A.; Waugh, J. S.; Seyferth, D. *J. Am. Chem. Soc.* **1961**, *83*, 1306–1307.
22. Zefirov, N. S.; Makhan'kov, D. I. *Chem. Rev.* **1982**, *82*, 615–624.
23. (a) Matveeva, E. D.; Podrugina, T. A.; Zefirov, N. S. *Mendeleev Commun.* **1998**, 21–22; (b) Grinblat, J.; Ben-Zion, M.; Hoz, S. *J. Am. Chem. Soc.* **2001**, *123*, 10738–10739; (c) Matveeva, E. D.; Podrugina, T. A.; Tishkovskaya, E. V.; Zefirov, N. S. *Mendeleev Commun.* **2003**, 260–262; (d) Matveeva, E. D.; Podrugina, T. A.; Sandakova, N. G.; Zefirov, N. S. *Zh. Org. Khim.* **2004**, *40*, 1517–1521 (Russ.); *Russ. J. Org. Chem.* **2004**, *40*, 1469–1473 (Engl. Transl.).
24. (a) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 6273–6284; (b) Glukhovtsev, M. N.; Pross, A.; Schlegel, H. B.; Bach, R. D.; Radom, L. *J. Am. Chem. Soc.* **1991**, *118*, 11258–11264; (c) Cyr, D. M.; Scarton, M. G.; Wiberg, K. B.; Jonson, M. A.; Nonose, S.; Hirokawa, J.; Tanaka, H.; Kondow, T.; Morris, R. A.; Viggiano, A. A. *J. Am. Chem. Soc.* **1995**, *117*, 1828–1832.
25. Binger, P.; Brinkmann, A.; Wedemann, P. *Synthesis* **2002**, 1344–1346.
26. Dolbier, W. R.; Riemann, M. J.; Akiba, K.; Bertrand, M.; Bezaguet, A.; Santelli, M. *J. Chem. Soc. D* **1970**, 718–719.
27. Hamdouchi, C.; Topolski, M.; Goedken, V.; Walborsky, H. M. *J. Org. Chem.* **1993**, *38*, 3148–3155.
28. Bee, L. K.; Everett, J. W.; Garratt, P. J. *Tetrahedron* **1977**, *33*, 2143–2150.
29. Arora, S.; Binger, P. *Synthesis* **1974**, 801–803.
30. Kuznetsova, T. S.; Averina, E. B.; Kokoreva, O. V.; Zefirov, A. N.; Grishin, Y. K.; Zefirov, N. S. *Zh. Org. Khim.* **2000**, *36*, 228–233 (Russ.); *Russ. J. Org. Chem.* **2000**, *36*, 205–210 (Engl. Transl.).
31. Schweizer, E. E.; Berninger, C. J.; Thompson, G. J. *J. Org. Chem.* **1968**, *33*, 336–339.
32. Donskaya, N. A.; Akhachinskaya, T. V.; Shabarov, Y. S. *Zh. Org. Khim.* **1976**, *12*, 1596–1597 (Russ.); *J. Org. Chem. USSR* **1976**, *12*, 1572–1573 (Engl. Transl.).
33. Lukin, K. A.; Zefirov, N. S. *Zh. Org. Khim.* **1987**, *23*, 2548–2552 (Russ.); *J. Org. Chem. USSR* **1987**, *23*, 2249–2252 (Engl. Transl.).
34. Compounds **8b**, **10b**, **21**, **22**, **25** are rather unstable and due to this fact satisfactory elemental analyses were not obtained for them and these compounds were characterized by NMR and mass spectra.
35. Akhachinskaya, T. V.; Grishin, Y. K.; Donskaya, N. A.; Roznyatovskii, V. A.; Shulishov, E. V.; Yusipovich, N. F.; Shabarov, Y. S. *Zh. Org. Khim.* **1987**, *23*, 2354–2364 (Russ.); *J. Org. Chem. USSR* **1987**, *23*, 2076–2085 (Engl. Transl.).