Synthesis of alicyclic derivatives of spiropentane based on 1,5-cyclooctadiene

T. S. Kuznetsova, O. V. Eremenko, O. V. Kokoreva, G.V. Zatonsky, and N. S. Zefirov*

M. V. Lomonosov Moscow State University, Department of Chemistry, Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: 007 (095) 939 0290

Methods for the synthesis of alicyclic derivatives of spiropentane by [1+2] cycloaddition of halo- and dihalocarbenes to 1,5-cyclooctadiene followed by dehydrohalogenation and cyclopropanation of the olefins formed are described.

Key words: polyspirocyclopropanes, alicyclic spiropentanes, cyclosubstituted triangulanes.

Spiropentane has a very high strain energy that is estimated to be 63 Kcal mol^{-1}.[1] The introduction of a spiropentane fragment into cycles of various sizes results in the appearance of additional strain and in the formation of strained polycyclic compounds, which are traditionally of high interest to chemists.[1–3] More than 30 years ago L. Skattebol[4] reported the synthesis of tricyclo[4.1.0.0^{1,3}]heptane by intramolecular [1+2] cycloaddition of γ-alkenylcyclopropylidene. Some derivatives of tricycloheptane have also been obtained in a similar way.[5–7] However, attempts to use this approach for the synthesis of other cyclic spiropentanes appear to have been unsuccessful. For example, the reaction of σ-alkenyldibromocyclopropane with methyl lithium afforded solely the corresponding allene,[8] and tricyclo[5.1.0.0^{1,3}]octane was not long ago obtained by a rather difficult method from 7-methylenetricyclo[4.1.0.0^{1,3}]heptane.[9] This reaction is a specific one and cannot be used for the synthesis of other polycyclic compounds.

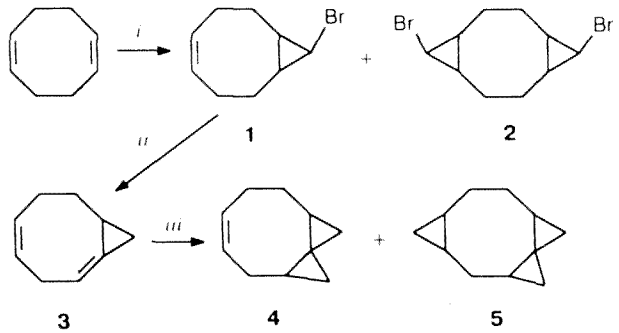
However, the development of methods for the synthesis of alicyclic spiropentane compounds is of great importance for the solution of synthetic problems in the chemistry of a new unique class of hydrocarbons, triangulanes.[10–12] We have proposed a methodology for sequential peripheral cyclopropanation of cycloolefins and have shown that tricyclo[7.1.0.0^{1,3}]decane is readily obtained by a three-step synthesis, *i.e.*, bromocyclopropanation of cyclooctene followed by dehydrobromination and cyclopropanation.[13,14] The proposed method appeared to be universal for the synthesis of a new class of highly strained polycyclic compounds, cyclosubstituted triangulanes.[15]

The goal of this work was to synthesize complex polycyclic structures containing a spiropentane fragment in the main cycle using the accessible olefin, 1,5-cyclooctadiene, and the well-developed procedures of [1+2] cycloaddition of carbenes to olefins.

We have found that the synthetic approach based on bromocyclopropanation of 1,5-cyclooctadiene can be successfully used for the synthesis of alicyclic spiropentanes.

Bromocyclopropanation of 1,5-cyclooctadiene by dibromomethane in the presence of sodium bis(trimethyl)silylamide affords monobromide **1** as a mixture of *cis*- and *trans*-isomers in a 20 : 1 ratio (in 35 % yield) and dibromide **2** (in 5 % yield). The yield of the latter is increased to 35 % when bromide **1** is repeatedly introduced into bromocyclopropanation. Dehydrobromination of compound **1** easily affords diene **3**. Cyclopropanation of **3** with an excess of diazomethane in the presence of palladium diacetate gives a mixture of the adducts of mono- and bis-cycloaddition (**4** and **5**) in an 8 : 1 ratio (according to the GLC data), and the ^{1}H NMR spectrum of the mixture does not contain the signals of protons typical of the methylenecyclopropane fragment, which confirms the primary formation of olefin **4**. Diene **3** is thermally unstable and readily under-

Scheme 1



Reagents: *i*, $CH_2Br_2/[(CH_3)_3Si]_2NNa$;
ii, $Bu^tOK/DMSO$;
iii, $CH_2N_2/Pd(OAc)_2$

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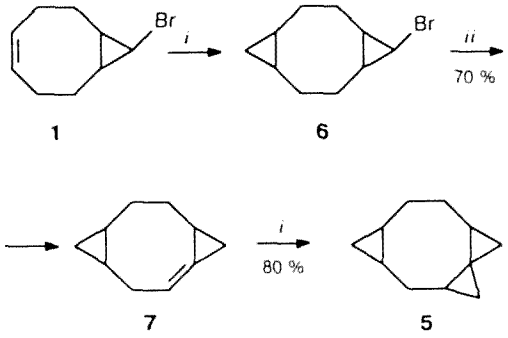
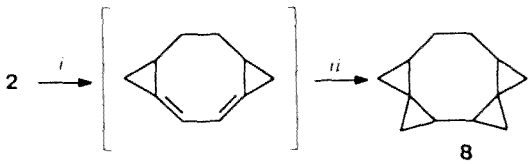
goes isomerization to cyclononatriene,[13] therefore, for the synthesis of hydrocarbon **5**, another method has been chosen, which excludes the presence of two multiple bonds in the eight-membered cycle of the molecule. To achieve this goal, monobromide **1** was first cyclopropanated and then dehydrobrominated to form olefin **7**, subsequent cyclopropanation of which afforded the same tetracyclic hydrocarbon **5**.



Reagents: *i*, $CH_2N_2/Pd(OAc)_2$; *ii*, Bu^tOK/DMSO

Hydrocarbon **5** obtained is a mixture of two isomers in a 4 : 1 ratio differing in the orientation of the isolated cyclopropane fragment. The isomers were isolated in an individual state by preparative GLC and fully characterized.

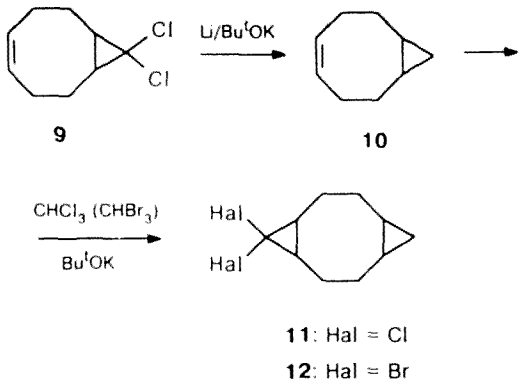
Dehydrobromination of dibromide **2** afforded a mixture of olefins, which was cyclopropanated with an eightfold excess of diazomethane without isolation, and the mixture of hydrocarbons obtained was separated by preparative GLC. In this case, the main reaction product isolated in ~25 % yield with respect to the initial dibromide was pentacyclo[9.1.0.0^{1,3}.0^{4,6}.0^{6,8}]dodecane **8**, the structure of which was confirmed by elemental analysis and ^1H and ^{13}C NMR spectroscopy involving two-dimensional spectroscopy.



Reagents: *i*, Bu^tOK/DMSO; *ii*, $CH_2N_2/Pd(OAc)_2$

Only six signals are observed in the ^{13}C NMR spectrum, which is explained by the elements of symmetry present in molecule **8**.

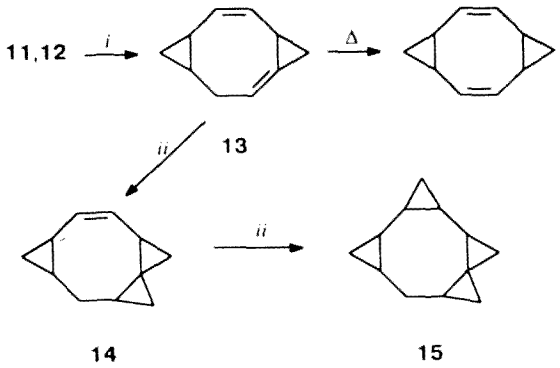
Another method for synthesizing alicyclic spiropentanes is based on addition of dihalocarbenes to 1,5-cyclooctadiene. The addition of dichlorocarbenes to 1,5-cyclooctadiene according to the Makosza method[16] gives monoadduct **9** in a high yield, and the complete reduction of dichloride **9** with lithium in *tert*-butanol affords key cycloolefin **10** in 75 % yield. The combination of these two reactions is essentially the two-step selective cyclopropanation of 1,5-cyclooctadiene.



11: Hal = Cl

12: Hal = Br

Olefin **10** was transformed into the previously unknown dichloride **11** (in the presence of dry KOH at room temperature, yield 57 %) or into dibromide **12** (by the Doering method,[17] yield 65 %), which were isolated as mixtures of *cis*- and *trans*-isomers. Their structures were confirmed by spectral methods and the microanalysis data. Both bishalides **11** and **12** can be dehydrohalogenated by potassium *tert*-butoxide in DMSO to form diene **13**, which was isolated in ~40 % yield by high vacuum distillation without heating.



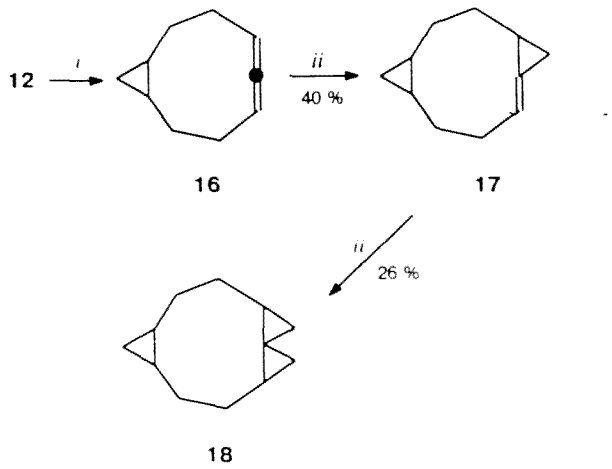
Reagents: *i*, Bu^tOK/DMSO; *ii*, $CH_2N_2/Pd(OAc)_2$

The ^{13}C NMR spectral data correspond to the structure of diene **13**. Four signals are present in the olefin part of the spectrum. Two of them, at δ 132.5 and 134.1, are assigned to the signals of the usual double bond, and the signals at δ 116.8 (the methylene carbon atom) and δ 126.9 (the quaternary carbon atom) belong to the methylenecyclopropane fragment. On heating, diene **13** readily undergoes isomerization with the migration of the double bond to form *cis*-tricyclo[7.1.0.0^{4,6}]diene-2,7 identical to the corresponding component of the mixture of hydrocarbons obtained by cyclopropanation of cyclooctatetraene.[18] Cyclopropanation of diene **13** with excess diazomethane in the presence of palladium

diacetate proceeds by several steps. The methylenecyclopropane double bond alone is cyclopropanated in the first step to form monoadduct **14**; subsequent cyclopropanation of **14** affords alicyclic hydrocarbon **15** containing a spiropentane fragment in the eight-membered cycle.

The ^{13}C NMR spectrum of olefin **14** contains two signals of CH groups at δ 133.01 and 135.78 corresponding to the ordinary double bond, and a signal at δ 17.78 typical of the spiro carbon atom. The ^{13}C NMR spectrum of hydrocarbon **15** has 12 signals including one signal of the CH_2 group of the eight-membered cycle at δ 27.46 and one signal of the quaternary spiro carbon atom at δ 15.66 indicating that only one of the possible isomers of hydrocarbon **15** is isolated from the reaction mixture.

One more synthetic approach to alicyclic spiropentanes is the synthesis of the allene derivative from dibromide **12** by the reaction with methyl lithium followed by cyclopropanation of allene **16** formed with an excess of diazomethane in the presence of palladium diacetate.



Reagents: *i*, MeLi, −30 °C; *ii*, $CH_2N_2/Pd(OAc)_2$

The ^1H and ^{13}C NMR spectral data of allene **16** indicate the absence of elements of symmetry in this molecule. For example, the ^{13}C NMR spectrum contains 10 signals; the presence of the signals of two CH groups at δ 88.7 and 93.3 and the signal of the quaternary cumulene carbon atom at δ 207.5 confirms the formation of the allene structure. In addition, the ^1H NMR spectrum contains two multiplets at δ 5.25 and 5.35, which are assigned to the protons of the cumulene fragment that also indicates the absence of symmetry in molecule **16**. Cyclopropanation of allene **16** with diazomethane (in a 8 : 1 molar ratio) proceeds with the formation of monoadduct **17** in 40 % yield; subsequent cyclopropanation of **17** with an eightfold excess of diazomethane affords spiropentane **18** involved in the nine-membered cycle. This hydrocarbon was isolated by preparative GLC as a mixture of two isomers in 26 % total yield.

Thus, we have developed the synthetic approaches to the preparation of alicyclic spiropentanes based on 1,5-cyclooctadiene.

Experimental

^1H and ^{13}C NMR spectra were recorded on Tesla BS-467 (60 MHz), Bruker AM-300 (300 MHz), and Varian VXR-400 (400 MHz) instruments. Mass spectra were obtained on Varian MAT 311 A and Varian MAT MX 1321 A instruments. GLC analysis was carried out on a Chrom-5 instrument with flame-ionizing detector, 3000×5 mm column, E-301 liquid phase (15 % on Inerton AW), nitrogen as the carrier gas, 40—60 mL min^{-1}. Preparative separation of hydrocarbons was carried out on a PAKhV-08 instrument with catharometer as the detector, 3000×5 mm column, E-301 liquid phase (15 % on Inerton AW), helium as the carrier gas, 80—120 mL min^{-1}. All the solvents and reagents were purified and dried by standard procedures.

9-Bromobicyclo[6.1.0]nonene-4 (1) and 5,10-dibromotricyclo[7.1.0.0^{4,6}]decane (2). Methylene bromide (1.45 mL, 20 mmol) was added dropwise to a mixture of 1,5-cyclooctadiene (4.3 g, 40 mmol) and $[(CH_3)_3Si]_2NNa$ (3.6 g, 20 mmol) in abs. pentane (10 mL) at −20 °C with vigorous stirring. After that, the reaction mixture was stirred for 1.5 h, and ice water was added. The organic layer was separated, and the aqueous layer was extracted with pentane. The extract was washed with water and extracted with $MgSO_4$. The solvent was evaporated, and the residue was distilled *in vacuo* to afford 1.4 g (36 %) of bromide **1** as a mixture of two isomers in a 20 : 1 ratio, b.p. 78—80 °C (2 Torr),[19] and 0.2 g (5 %) of dibromide **2** as a mixture of two isomers in a 6 : 1 ratio (according to the GLC data), b.p. 110—115 °C (2 Torr), m.p. 74—76 °C (from pentane). ^1H NMR (300 MHz, $CDCl_3$), δ: 1.1—1.23 (m, 4 H); 1.55—1.73 (m, 4 H); 1.95—2.1 (m, 4 H); 3.34 (t, 2 H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 17.82 (4 CH); 22.87 (4 CH_2); 32.69 (2 CHBr). MS (I_{rel} (%)), *m/z*: 292, 294, 296 [M^+] (1), 213 (20), 133 (77), 119 (21), 105 (27), 91 (85), 79 (61), 67 (100), 53 (34). Starting from bromide **1** (7.4 g, 37 mmol), 1.9 g (35 %) of dibromide **2**, completely identical to the previously described one, was obtained.

10,10-Dichlorotricyclo[7.1.0.0^{4,6}]decane (11). A solution of $CHCl_3$ (11 mmol) in methylene chloride was added dropwise to a mixture of powdered KOH (1.23 g, 22 mmol), TEBA (0.1 g), and olefin **10** (1.2 g, 10 mmol) in CH_2Cl_2 at 0 °C with vigorous stirring for 2 h. The mixture was stirred for 4 h at −20 °C and treated with ice water (150 mL), the organic layer was separated, and the aqueous layer was extracted with ether. The solvent was evaporated, and the residue was distilled *in vacuo* to afford 1.17 g (57 %) of dichloride **11** as a mixture of isomers in a 3 : 1 ratio (according to the GLC data), b.p. 95—100 °C (2 Torr). ^1H NMR (300 MHz, $CDCl_3$), δ: −0.2—0.05, 0.80—0.95, 1.20—1.40, 1.52—1.61, 1.63—1.70, 1.76—1.84, 2.07—2.34 (all multiplets). ^{13}C NMR (300 MHz, $CDCl_3$), δ: 13.61 (CH_2), 14.13 (CH_2), 14.59 (CH), 16.89 (CH), 22.90 (CH_2), 25.11 (CH_2), 26.46 (CH_2) 27.92 (CH_2), 32.43 (CH), 35.89 (CH), 66.80 (C), 67.10 (C). Found (%): C, 57.68; H, 6.59. $C_{10}H_{14}Cl_2$. Calculated (%): C, 58.54; H, 6.83.

10,10-Dibromotricyclo[7.1.0.0^{4,6}]decane (12). $CHBr_3$ (1.05 mL, 12 mmol) was added dropwise to a mixture Bu^tOK (3.13 g, 28 mmol) in abs. pentane and olefin **10** (1.68 g, 14 mmol) at 0 °C with vigorous stirring. The mixture was

stirred for 4 h at ~20 °C, and two volumes of ice water were added. The organic layer was separated, and the aqueous layer was extracted with ether. The extracts were dried, the solvent was evaporated, and the residue was distilled *in vacuo* to afford 2.6 g (65 %) of dibromide **12** as a mixture of isomers in a 3 : 1 ratio (according to the GLC data), b.p. 110—111 °C (2 Torr). ^{1}H NMR (300 MHz, CD_2Cl_2), δ: −0.1—0.2, 0.6—0.75, 0.80—0.95, 1.15—1.30, 1.40—1.56, 1.65—1.77, 1.85—1.95 (all multiplets). ^{13}C NMR (CD_2Cl_2), δ: 12.53 (CH_2), 13.21 (CH_2), 13.75 (CH), 17.80 (CH), 24.37 (CH_2), 25.35 (CH_2), 26.48 ($2CH_2$), 32.41 (CH), 35.81 (CH), 38.04 (C), 40.64 (C). Found (%): C, 40.55; H, 4.68. $C_{10}H_{14}Br_2$. Calculated (%): C, 40.85; H, 4.80.

General procedure for dehydrohalogenation. Bromide (12 mmol) or dibromide (dichloride) (6 mmol) was added to a suspension of Bu^{t}OK (6.7 g, 60 mmol) in abs. DMSO with vigorous stirring in inert atmosphere. The reaction mixture was stirred for 6 h (15 h for dibromide **2**) and treated with ice water (100 mL). Pentane (50 mL) was then added, the organic layer was separated, and the aqueous layer was extracted with pentane. The extracts were thoroughly washed with water and dried. The pentane extracts were carefully concentrated. Olefin **7** was isolated by distillation, diolefin **13** was purified by flesh-distillation *in vacuo* (10^{-2}—10^{-3} Torr) at ~20 °C, and diolefin **3** was used without isolation from the reaction mixture.

Bicyclo[6.1.0]nona-1,4-diene (3). Starting from bromide **1** (3.3 g, 16 mmol), diene **3** (1.28 g, 65 %) was obtained. ^{1}H NMR (60 MHz, CCl_4), δ: −0.53—0.0 (1 H), 0.55—1.00 (2 H), 1.00—2.5 (6 H), 5.1—5.5 (2 H), 5.75—5.9 (1 H) (all multiplets).

Tricyclo[7.1.0.0^{4,6}]dec-1-ene (7). Starting from bromide **6** (1.5 g, 7 mmol), olefin **7** (0.65 g, 70 %) was obtained as a mixture of two isomers in a 6 : 1 ratio (according to the GLC data), b.p. 42—45 °C (2 Torr). ^{1}H NMR (200 MHz, CD_2Cl_2), δ: −0.25 to −0.1 and −0.1 to 0.1 (1 H), 0.65—0.85 (3 H), 0.95—1.15 (1 H), 1.40—1.50 (2 H), 1.62—1.80 (2 H), 1.90—2.00 (1 H), 2.18—2.36 (2 H), 2.50—2.60 (1 H), 5.94—5.98, and 6.08—6.15 (1 H) (all multiplets).

Tricyclo[7.1.0.0^{4,6}]deca-1,7-diene (13). Starting from dichloride **11** (2 g, 10 mmol), diene **13** (0.5 g, 39 %) was obtained. ^{1}H NMR (300 MHz, CD_2Cl_2, −30 °C), δ: 0.02 to 0.00 (1 H), 0.8—1.26 (3 H), 1.40—1.70 (2 H), 2.40—2.50 (1 H), 2.70—2.87 (1 H), 3.34—3.50 (1 H), 5.40—5.48 (2 H), 5.66—5.90 (1 H) (all multiplets). ^{13}C NMR (CD_2Cl_2), δ: 11.08 (CH_2), 11.54 (CH_2), 16.05 (CH), 16.48 (CH), 18.82 (CH), 32.70 (CH_2), 116.99 (CH), 117.04 (CH), 127.12 (CH), 132.81 (C).

Starting from dibromide **12** (2.9 g, 10 mmol), diene **13** (0.46 g, 35 %), completely identical to the described above, were obtained.

General procedure for cyclopropanation of olefins. An ethereal solution of diazomethane prepared from *N*-nitroso-*N*-methylurea (4 g) was added dropwise at −4 to 0 °C to a mixture of olefin (5 mmol) (2.5 mmol in the case of **3**) and palladium diacetate (30 mg). The reaction mixture was filtered through a silica gel, the solvent was evaporated, and hydrocarbons **4**, **5**, and **16**—**18** were isolated by preparative GLC, and bromide **6** by distillation *in vacuo*.

Tricyclo[7.1.0.0^{1,3}]decene-5 (4) and tetracyclo[8.1.0.0^{1,3}.0^{5,7}]undecane (5). Starting from diolefin **3** (2.88 g, 24 mmol), hydrocarbon **4** (2.2 g, 65 %) and hydrocarbon **5** (0.39 g, 11 %) as a mixture of two isomers in a 4 : 1 ratio, were obtained. The isomers were separated by preparative GLC.

Compound **4**. ^{1}H NMR (200 MHz, CD_2Cl_2), δ: −0.35 to 0.05 (1 H), 0.10—0.45 (2 H), 0.61—0.98 (4 H), 1.00—1.52 (3 H), 1.60—2.62 (2 H), 5.20—5.54 (2 H) (all multiplets). ^{13}C NMR (CD_2Cl_2), δ: 5.86 (CH_2), 10.19 (CH_2), 17.28 (CH), 18.74 (CH), 19.19 (C), 25.15 (CH_2), 30.28 (CH_2), 33.30 (CH_2), 127.71 (CH), 129.32 (CH).

Compound **5**. *Major isomer*. ^{1}H NMR (300 MHz, CD_2Cl_2), δ: −0.247 to −0.18 (m, 1 H), 0.14—0.34 (m, 1 H), 0.50 (t, 1 H, J = 3.75), 0.0—1.00 (m, 8 H), 1.21—1.32 (m, 1 H), 1.33—1.43 (m, 1 H), 1.95—2.10 (m, 1 H), 2.36—2.47 (m, 1 H), 2.58—2.66 (dt, 1 H, J_1 = 3.4, J_2 = 3.4 Hz). ^{13}C NMR (CD_2Cl_2), δ: 12.41 (CH_2), 14.69 (CH_2), 17.03 (CH), 17.77 (CH_2), 19.13 (CH), 19.22 (CH), 19.55 (C), 19.78 (CH), 28.62 (CH_2), 33.83 (CH_2), 36.18 (CH_2). *Minor isomer*. ^{1}H NMR (300 MHz, CD_2Cl_2), δ: −0.30 to −0.25 (m, 1 H), 0.32—0.36 (m, 1 H), 0.45—0.83 (m, 4 H), 0.88—0.95 (m, 3 H), 1.28—1.43 (m, 5 H), 1.85—1.96 (m, 1 H), 2.07—2.23 (m, 1 H), 2.31—2.41 (m, 2 H). ^{13}C NMR (CD_2Cl_2), δ: 9.18 (CH_2), 10.72 (CH_2), 10.98 (CH), 14.76 (CH), 15.22 (CH_2) 15.87 (CH), 17.60 (CH), 22.14 (CH_2), 22.94 (C), 28.73 (CH_2), 30.15 (CH_2). MS, m/z (I_{rel} (%)): 148 [M+] (5), 133 (27), 119 (34), 105 (76), 91 (100), 67 (44), 53 (13). Found (%): C, 88.90; H, 10.90. $C_{11}H_{16}$. Calculated (%): C, 89.12; H, 10.88. Starting from olefin **7** (0.26 g, 2 mmol), hydrocarbon **5** (0.23 g, 80 %) as a mixture of two isomers in a 4 : 1 ratio, completely identical to the described above, was obtained.

10-Bromotricyclo[7.1.0.0^{4,6}]decane (6). Starting from bromide **1** (1.7 g, 8.4 mmol), bromide **6** (1.45 g, 80 %) as a mixture of isomers in a 4 : 1 ratio (according to the GLC data) was obtained, b.p. 92—93 °C (2 Torr). ^{1}H NMR (300 MHz, CD_2Cl_2), δ: −0.02 to −0.08 and 0.5—0.75 (two m, 2 H), 0.08—0.97 (m, 4 H), 1.20—1.44 and 1.90—2.32 (two m, 8 H), 3.22 and 3.35 (two t, 1 H, J = 6.6 Hz). ^{13}C NMR (CD_2Cl_2), δ: 13.06 (CH_2), 13.40 (CH_2), 14.46 (CH), 18.20 (CH), 18.56 (CH), 22.07 (CH), 23.53 (CH_2), 25.66 (CH_2), 26.45 (CH_2), 28.18 (CH_2), 30.28 (CH_2), 31.43 (CHBr), 33.91 (CHBr). MS, m/z (I_{rel} (%)): 214, 216 [M$^+$] (3), 135 (56), 120 (42), 105 (41), 91 (77), 79 (43), 67 (100), 53 (30).

Tetracyclo[8.1.0.0^{1,3}.0^{6,8}]undec-4-ene (14). Starting from diolefin **13** (0.8 g, 6 mmol), hydrocarbon **14** (0.54 g, 62 %) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$), δ: −0.08 (1 H), 0.60 (1 H), 0.66—0.75 (3 H), 1.00 (2 H), 1.20—1.30 (2 H), 1.30—1.40 (1 H), 1.80 (1 H), 2.30 (1 H), 5.55—5.65 (2 H) (all multiplets. ^{13}C NMR (CD_2Cl_2), δ: 7.65 (CH_2), 10.45 (CH_2), 13.10 (CH_2), 14.35 (CH), 15.44 (CH), 16.60 (CH), 16.97 (CH), 17.78 (C), 28.09 (CH_2), 134.01 (CH), 135.78 (CH).

Pentacyclo[9.1.0.0^{1,3}.0^{4,6}.0^{7,9}]dodecane (15). Starting from alkene **14** (0.4 g, 2.7 mmol), hydrocarbon **15** (0.04 g, 10 %) was obtained. ^{1}H NMR (300 MHz, CD_2Cl_2), δ: −0.30 — 0.0 (1 H), 0.15—0.25 (2 H), 0.36—0.44 (1 H), 0.45—0.66 (1 H), 0.75—0.85 (2 H), 0.90—1.10 (2 H), 1.30—1.15 (2 H), 2.4 (1 H) (all multiplets) ^{13}C NMR (CD_2Cl_2), δ: 7.52 (CH_2), 12.52 (CH_2), 14.12 (CH_2), 15.55 (CH_2), 15.66 (C), 15.99 (CH), 16.41 (CH), 17.31 (CH), 18.30 (CH), 18.74 (CH), 27.46 (CH_2).

Tricyclo[8.1.0.0^{5,7}]undec-1-ene (17). Starting from allene **16** (0.67 g, 5 mmol), olefin **17** (0.29 g, 40 %) was obtained. ^{1}H NMR (60 MHz, CD_2Cl_2), δ −0.4 (1 H), 0.50—2.50 (13 H), 5.90 (1 H) (all multiplets). ^{13}C NMR (CD_2Cl_2), δ: 7.94 (CH_2), 9.20 (CH_2), 17.83 (CH), 17.88 (CH), 19.64 (CH), 23.65 (CH_2), 28.80 (CH_2), 33.05 (CH_2), 34.17 (CH_2), 118.00 (CH), 125.29 (C).

Tetracyclo[9.1.0.0^{1,3}.0^{6,8}]dodecane (18). Starting from olefin **17** (115 mg, 0.78 mmol), triangulane **18** (30 mg, 26 %) as

a mixture of isomers in a 6 : 1 ratio (according to the GLC data) was obtained. ^{13}C NMR (CD_2Cl_2), δ: 4.42 (CH_2), 4.45 (CH_2), 9.04 (CH_2), 9.13 (CH_2), 10.03 (CH_2), 10.88 (CH), 11.41 (CH_2), 11.75 (CH_2), 12.35 (CH_2), 16.05 (CH), 16.21 (C), 17.31 (CH), 19.53 (CH), 22.49 (CH), 23.64 (CH_2), 26.86 (CH_2), 29.69 (CH_2), 30.85 (CH_2), 32.22 (CH_2).

Pentacyclo[9.1.0.0^{1,3}.0^{4,6}.0^{6,8}]dodecane (8). Cyclopropanation of diolefin obtained by dehydrobromination of dibromide **2** (1 g, 3.4 mmol), afforded 0.15 g of a mixture of hydrocarbons, which was separated by preparative GLC. The main fraction was hydrocarbon **8** (0.1 g, 25 %). ^1H NMR (300 MHz, $CDCl_3$), δ: 0.23 (t, 2 H, J = 3.9 Hz), 0.58—0.64 (m, 2 H), 0.73—0.78 (m, 4 H), 0.89—1.08 (m, 2 H), 1.15—1.30 (m, 4 H), 2.46—2.50 (m, 1 H), 2.51—2.55 (m, 1 H). ^{13}C NMR ($CDCl_3$), δ: 7.84 (C-7, C-12), 10.56 (C-2, C-5), 12.49 (C-9, C-11), 16.90 (C-1, C-6), 17.93 (C-3, C-4), 31.43 (C-9, C-10). MS, m/z (I_{rel} (%)): 160 [M+] (10), 145 (29), 131 (33), 119 (41), 105 (77), 91 (100), 79 (80), 67 (45), 53 (27). Found (%): C, 89.73; H, 10.00. $C_{12}H_{16}$. Calculated (%): C, 89.94; H, 10.06.

Bicyclo[7.1.0]decad-4,5-iene (16). A 1.1 *N* ethereal solution of MeLi (15 mmol) was added dropwise to a solution of dibromide **12** (2.92 g, 10 mmol) in abs. ether (10 mL) at −30 °C for 0.5 h. The mixture was stirred for 1 h at −30 °C, and then water (100 mL) was added. The organic layer was separated, and the aqueous layer was extracted with ether. The extracts were dried, the solvent was carefully evaporated, and the residue was distilled *in vacuo* to afford 0.65 g (50 %) of allene **16**, b.p. 35—40 °C (3 Torr). ^1H NMR (300 MHz, CD_2Cl_2), δ: −0.45 to −0.40 (1 H), 0.45—0.60 (2 H), 0.70—0.80 (1 H), 1.02—1.12 (1 H), 1.30—1.50 (1 H), 1.80—2.00 (2 H), 2.04—2.20 (3 H), 2.22—2.36 (1 H), 5.20—5.30 (1 H), 5.32—5.40 (1 H) (all multiplets). ^{13}C NMR (CD_2Cl_2), δ: 8.27 (CH_2), 18.55 (CH), 19.51 (CH), 24.71 (CH_2), 26.18 (CH_2), 26.76 (CH_2), 31.66 (CH_2), 88.74 (CH), 93.27 (CH), 207.5 (C).

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