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Synthesis and Stereochemistry of Novel Dibrominated 1,5-Dioxaspiro[5.5]undecane Derivatives

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Summary. The synthesis and stereochemistry of new dibrominated spiro-1,3-dioxane derivatives are reported. Investigations by means of NMR methods and single crystal X-ray diffraction for two compounds revealed the high regio- and diastereoselectivity of the bromination reaction of some new spiro-1,3-dioxanes and the asymmetric induction of the chiral carbon atom located in the spiro skeleton.

Keywords. Spiro compounds; Diastereoselective bromination; X-Ray structure determination; Conformation; NMR Spectroscopy.

Introduction

Recent studies [1–3] of the bromination reaction of spiro-1,3-dioxanes revealed the high regio- and diastereoselectivity of this process. The reaction of some 1,5-dioxaspiro[5.5]undecane derivatives with bromine under conditions similar to those used in the bromination reaction of some 1,3-dioxolane derivatives [4–9] gives rise to a unique diastereomer (showing the bromine atoms in *trans* orientation) of the 7,11-dibrominated derivative [2]. The high stereoselectivity of the reaction has been observed in compounds both with or without chiral centers in the cyclohexane ring (Scheme 1). However, if the spirane exhibits a chiral center in its skeleton, this induces (with a very high selectivity) the configuration of the new chiral centers formed by the bromination reaction. Finally, only one dibrominated *trans*-diastereomer has been obtained (Scheme 1).

It has been considered to be of interest to investigate the selectivity of the bromination reaction on some new spiro compounds displaying the 1,5-dioxaspiro[5.5]undecane skeleton and showing chiral centers in a more hindered

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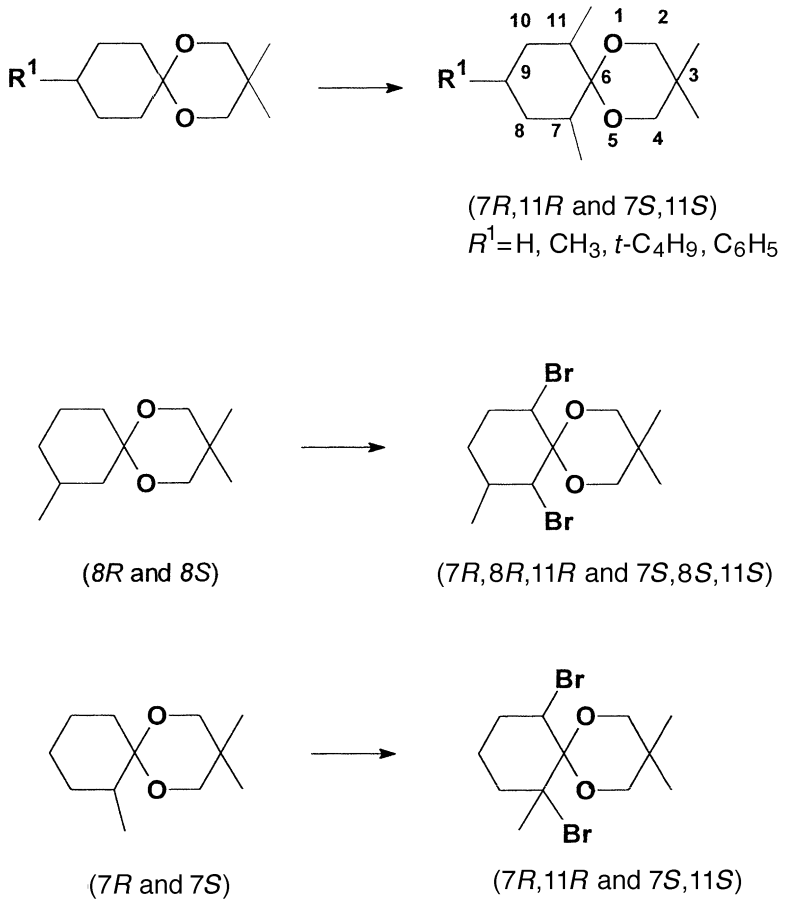


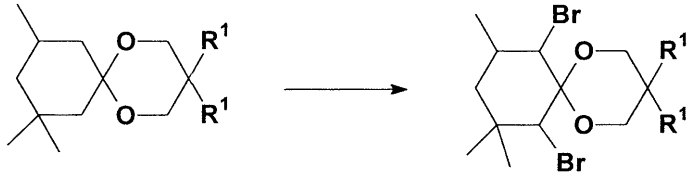
Scheme 1

cyclohexane ring as a useful itinerary to get 2,6-dibrominated alkylated cyclohexanones. Investigations on the influence of the selectivity of the bromination reaction on a chiral center located in the heterocycle have also been considered as relevant.

Results and Discussion

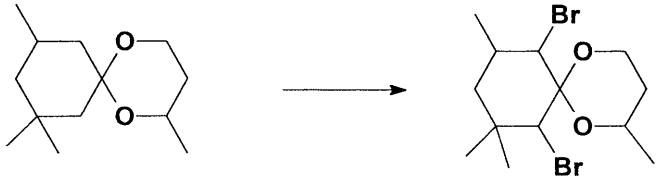
The dibromo-spiro-1,3-dioxanes were synthesized as usual by bromination of cyclic acetals (Scheme 2). Compounds **2** and **4** were obtained as unique diastereomers (7*R*, 10*R*, 11*R* and 7*S*, 10*S*, 11*S*); the configuration of the initial chiral center (C^{10}) of the unbrominated spirane determines the configurations of the other two chiral centers (C^7 and C^{11}) of the brominated compound as well as the helicity [10–14] of the spiro skeleton (Table 1).

The preference of the rings for the chair conformation and the axial or equatorial disposition of the substituents were deduced both from the crystal structure of **2** and from NMR investigations. The ORTEP diagram of **2** (Fig. 1) shows the equatorial orientation of the methyl group located in position 10 and the



1 $R^1 = H$ **2**

3 $R^1 = CH_3$ **4**



5 **6**

Scheme 2

Table 1. Configuration of chiral elements in **2**, **4**, and **6**

Compound	C^{10}	C^2	C^7	C^{11}	Helix
2	*R*	–	*R*	*R*	*M*
	S		*S*	*S*	*P*
4	*R*	–	*R*	*R*	*M*
	S		*S*	*S*	*P*
6(D_1)	*R*	*R*	*R*	*R*	*M*
	S	*S*	*S*	*S*	*P*
6(D_2)	*R*	*S*	*R*	*R*	*M*
	S	*R*	*S*	*S*	*P*

bromine atom in position 7 as well as the axial position of the bromine atom at C^{11}. The bond lengths, bond angles, and torsion angles are in the usual range [15, 16]. However, a flattening of the cyclohexane ring close to the spiro carbon atom and a modification of the bond angles of the carbon atom bearing the two methyl groups in order to decrease the strain of the structure were observed.

These dispositions of the bromine atoms were also deduced from ^{1}H NMR spectra using the values of the coupling constants of the proton attached to C^{11}. The signal belonging to this proton (**2**:$\delta = 4.53$, **4**:$\delta = 4.73$ ppm) is a pseudo-triplet (doublet of doublets with similar coupling constants; **2** and **4**: $^3J_{11e-10a} \approx^4 J_{11e-9e} = 2.3$ Hz). The long-range coupling between the equatorial protons in positions 9 and 11 is large because of the W disposition of the bonds H_{eq}-C(11)-C(10)-C(9)-H_{eq}.

The signal belonging to the axial proton in position 7 is a singlet (**2**: $\delta = 4.46$, **4**: $\delta = 4.57$ ppm) and does not show a long-range coupling with the equatorial proton in position 9. Furthermore, under normal recording conditions (no relaxation

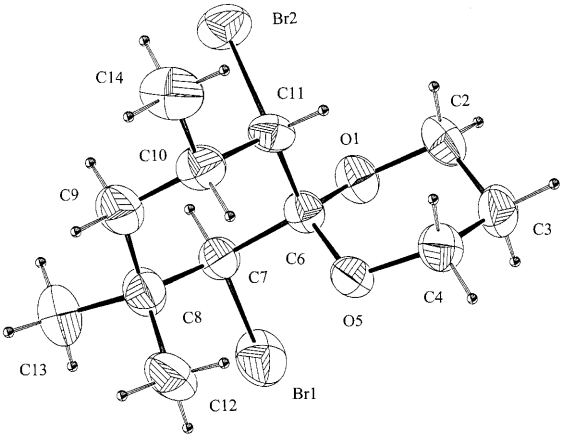
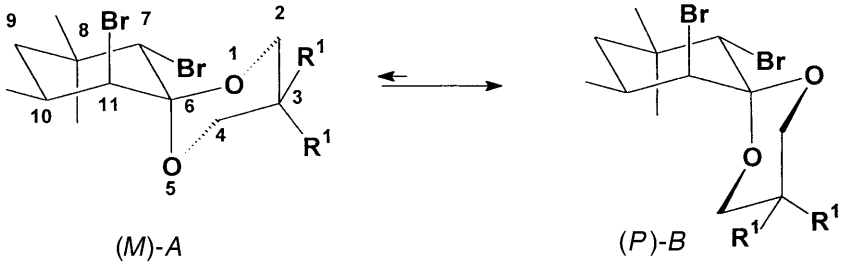


Fig. 1. X-Ray structure of **2**



Scheme 3

delay) a reduced intensity of its ^{1}H NMR signal (about 75% of the intensity of H-11 is observed due to its long relaxation time caused by its surroundings (quaternary carbons). Using a relaxation delay of 10 s renders the intensities of H-7 and H-11 equal.

Compounds **2** and **4** show anancomeric structures [17]. The conformational equilibration of the carbocycle is hindered by the methyl group at C^{10} (holding group), whereas the flipping of the heterocycle is hindered by the equatorial bromine atom in position 7, thus causing a shift of the characteristic equilibrium towards conformation B (Scheme 3).

The NMR spectra (Table 2) exhibit different signals for the axial and equatorial protons in positions 2 and 4 as well as for the axial and equatorial protons (methyl groups) in position 3 (compound **4**). Positions 2 and 4 are diastereotopic; the recorded values of the diastereotopicities (Table 2) are in the usual range [10–14].

Compound **6** was obtained as a mixture (≈1:1) of two diastereomers (the mixture of diastereomers of compound **5** obtained by acetalization of the corresponding racemic ketone and racemic 1,3-propanediol was used as the starting material). All chiral centers of the carbocycle (Table 1) exhibit the same configuration, whereas the chiral center belonging to the heterocycle can show both

Table 2. NMR data (δ/ppm) of **2**, **4**, and **6**

Compound	^{1}H						^{13}C		
	2*a*	4*a*	$\Delta\delta$	2*e*	4*e*	$\Delta\delta$	2	4	$\Delta\delta$
2	3.06	3.41	0.35	3.36	3.53	0.17	58.63	59.86	1.23
4	3.05	3.40	0.35	3.11	3.24	0.13	69.25	70.44	1.19
6(D_1)	3.15	3.42	0.27	–	3.58	–	67.13	65.63	−1.50
6(D_2)	3.45	3.08	−0.37	–	3.43	–	67.36	64.73	−2.63

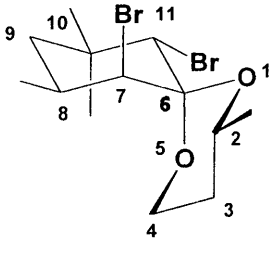
configurations generating the two obtained diastereomers of **6** (D_1: (2*R*, 7*R*, 10*R*, 11*R*/2*S*, 7*S*, 10*S*, 11*S*), D_2: (2*S*, 7*R*, 10*R*, 11*R*/2*R*, 7*S*, 10*S*, 11*S*); Scheme 4).

The two diastereomers were successfully separated by selective crystallization from ethanol. Their structures were deduced from single crystal X-ray diffraction of D_2 and by high resolution NMR spectra in solution.

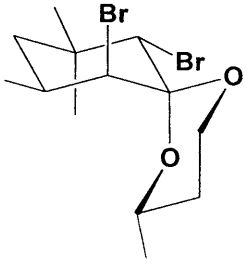
The ORTEP diagram of diastereomer D_2 (Fig. 2) shows an equatorial orientation of the methyl groups in positions 2 and 10 and of the bromine atom in position 7 and an axial orientation of the bromine atom in position 11. The analysis of bond lengths, bond angles, and main torsion angles shows a light flattening of the cyclohexane ring and small modifications of the bond angles and bond lengths involving the axial methyl group and the axial bromine atom in order to diminish the *syn*-axial interactions. Both diastereomers exhibit anancomeric structures.

The axial and equatorial position of bromine atoms were also deduced from the ^{1}H NMR signals belonging to the protons in positions 7 and 11. Thus, the signal of the equatorial proton in position 11 (D_1: $\delta = 4.57$, D_2: $\delta = 4.50$ ppm) exhibits a triplet-like signal (doublet of doublets with similar coupling constants: $^3J_{11e-10a} \approx {}^4J_{11e-9e} = 2.2$ Hz). The singlet belonging to the axial proton in position 7 (D_1: $\delta = 4.49$, D_2: $\delta = 4.46$ ppm) behaves as discussed for **2** and **4** with respect to its intensity, (about 75% of H-11).

The ^{1}H NMR spectrum of diastereomer D_1 (Fig 3a) exhibits for the axial and equatorial protons in position 4 two doublets of doublets of doublets. The signals were assigned using the values of the coupling constants with the vicinal axial and equatorial protons (position 3). The signal of the axial proton (less deshielded



(*P*)-D_1 (2*S*,7*S*,10*S*,11*S*)



(*P*)-D_2 (2*R*,7*S*,10*S*,11*S*)

Scheme 4

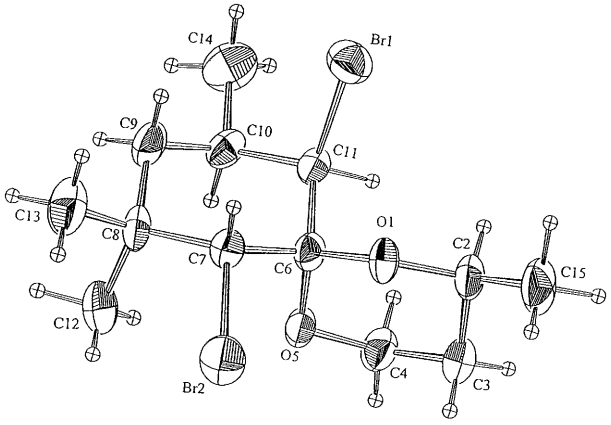


Fig. 2. X-Ray structure of **6** (D_2)

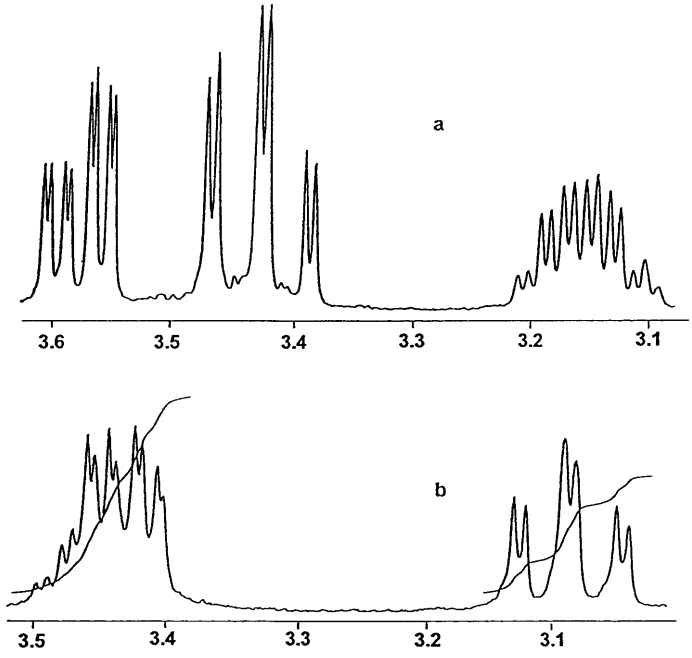


Fig. 3. ^{1}H NMR spectra (fragments) of diastereomers D_1 (a) and D_2 (b) of **6**

doublet of triplets, $\delta = 3.42$ ppm) displays two large and similar coupling constants resulting from coupling of this proton with the geminal equatorial and with the axial vicinal proton ($^3J_{3a-4a} \approx^2 J_{4e-4a} = 12.0$ Hz). A small coupling constant with the vicinal equatorial proton ($^3J_{3e-4a} = 2.3$ Hz) was observed.

The signal (ddd) belonging to the equatorial proton in position 4 is more deshielded ($\delta = 3.58$ ppm) and displays coupling constants of quite different values ($^2J_{4e-4a} = 12.0, ^3J_{4e-3a} = 5.2, ^3J_{4e-3e} = 1.5$ Hz) characteristic for an equatorial proton located in a chair 1,3-dioxane ring [15].

For the axial proton in position 2 a more shielded ($\delta = 3.15$ ppm) doublet of sextets (overlapped doublet of doublets of quarters; $^3J_{2a-3a} = 11.8$,$^3J_{2a-Me} = 6.0$,$^3J_{2a-3e} = 2.7$ Hz) was observed. The shape of the signal is due to the fact that the value of the vicinal axial-axial coupling constant ($^3J_{2a-3a} = 11.8$ Hz) is about twice as high as the value of the coupling constant with the protons of the equatorial methyl group ($^3J_{2a-Me} = 6.0$ Hz). The ^{1}H NMR spectrum of diastereomer D_2 (Figure 3b) exhibits two doubles of doublets of doublets for the protons in position 4. The less deshielded one ($\delta = 3.08$ ppm), which is overlapped a doublet of triplets (two coupling constants with large and similar values: $^2J_{4e-4a} \approx {}^3J_{4a-3a} = 12.0$ Hz) belongs to the axial proton, whereas the other signal ($\delta = 3.43$ ppm) displaying small vicinal coupling constants (characteristic for the coupling of vicinal equatorial-equatorial and equatorial-axial protons: $^3J_{4e-3e} = 1.6$ and $^3J_{4e-3a} = 5.2$ Hz) pertains to the equatorial proton. The signal of the equatorial proton is overlapped with the signal of the axial proton in position 2 ($\delta = 3.45$ ppm). The signal of this proton is an overlapped doublet of doublets of quartets resulting into a doublet of sextets.

The main difference between the ^{1}H NMR spectra of the two diastereomers consists in the different magnetic environment (δ values) of the axial protons in positions 2 and 4. In D_2 the axial proton in position 2 is close to the axial bromine atom in position 11 and is highly deshielded ($\delta = 3.45$ ppm), whereas in D_1 the axial proton in position 2 is not significantly deshielded by the axial bromine atom in position 11 ($\delta = 3.15$ ppm; $\Delta\delta_{D2-D1} = 0.30$ ppm). A similar influence is observed on the axial proton in position 4 which is more deshilded in diastereomer 1 ($\delta_1 = 3.42$ ppm, $\delta_2 = 3.08$ ppm, $\Delta\delta_{D1-D2} = 0.34$ ppm).

Conclusions

The bromination reaction of some derivatives of 8,8,10-trimethyl-1,5-dioxaspiro-[5.5]undecane showed a high diastereoselectivity, and only the isomers with *trans* bromine atoms and the same configuration for all chiral carbon atoms of the carbocycle were obtained. The configuration at the new chiral centers is induced by the configuration of the chiral carbon atom of the cyclohexane ring and is independent of the configuration of the chiral center of the 1,3-dioxane ring. All investigated compounds exhibit anancomeric structures with chair conformations for both six-membered rings.

Experimental

^{1}H and ^{13}CNMR spectra were recorded at room temperature using C_6D_6 as solvent in 5 mm tubes on a Bruker AM 400 (Varian Gemini 300) NMR spectrometer equipped with a dual ^{13}C-^{1}H (multinuclear) head operating at 400 (300) MHz for protons and 100 (75) MHz for carbon atoms. Melting points were measured with an Electrothermal melting point apparatus and are uncorrected.

Microanalyses (C, H, Br) were performed in the microanalytical laboratory of the University of Medicine and Pharmaceutics in Cluj-Napoca, Romania. Their results agreed favourably with the calculated values. The experimental conditions for the X-ray structure determinations of compounds **2** and **6** and details of the refinements are given in Table 3. The structural data were deposited at the Cambridge Crystallographic Date Center.

Table 3. Parameters of the crystallographic determinations[a] for **2** and **6** (D_2)

	Compound **2**	Compound **6** (D_2)
Color, shape	colorless prism	cololess prism
Crystal dimensions (mm	0.35×0.20×0.18	0.18×0.15×0.12
Crystal system/space group	monoclinic/$P2_1$/c	monoclinic/$P2_1$/c
a/Å	6.664(5)	6.405(3)
b/Å	20.370(5)	11.834(8)
cÅ	10.349(2)	19.704(2)
α/°		
β/°	97.86(2)	90.92(2)
γ/°		
V/Å^3	1386(1)	1493(1)
Z	4	4
D_{calc}/Mg · m^{-3}	1.705	1.646
μ_{calc}/cm^{-1}	58.28	53.662
θ_{max}/°	27	27
Scan mode	$\omega/2\theta$	$\omega/2\theta$
t_{max}/s	60	60
Index ranges	0.7/0.25/−13.13	0.7/0.14/−23.23
Reflns collected/unique reflns	3153/2900	3641/2119
Observed/parameters	2900/146	2119/221
$R/R_w/S_w$	0.051/0.133/1.037	0.037/0.036/1.237
Residual (eÅ^3, $\Delta\rho\leq$)	0.92	0.53

[a] Collected on automatic diffractometer CAD4 ENRAF-NONIUS with graphite monochromatized MoK_α radiation. The cell parameters are obtained by fitting 25 high-θ reflections. After *Lorenz* and polarization corrections [18] and analytical absorbtion corrections [19] the strucre of compound **2** was solved with SIR-97 [20] and the structure of compound **6** was solved with SIR92 [21] which reveal all nonhydrogen atoms of the structure. After anisotropic refinement, all hydrogen atoms are found with a *Fourier* difference; calc $w = 1/(\sigma^2(F_o^2) + (0.0951P)^2 + 0.1000P)$ where $P = F_o^2 + 2F_e^2/3$ and $w = 1/\sigma(F_0)^2 = (\sigma^2(I) + (0.04F_0^2)^2)^{-1/2}$

Compounds **2**, **4** *and* **6** (*general procedure*)

Spiro 1,3-dioxane **1**, **3** or **5** [14, 22] (0.1 mol) and 100 cm^3 dry diethyl ether (or CH_2Cl_2) were introduced in a four-necked flask equipped with a reflux condenser, a mechanic stirring system, a thermometer, and a dropping funnel. Br_2 (0.2 mol) was added dropwise to this stirred mixture cooled in an ice bath at 0–5°C, the ensuing reaction being monitored initially by the fading of the solution colour. After the addition of the Br_2, the ice bath was removed, and the stirring was continued for 1 h, the contents in the flask being allowed slowly to reach room temperature (20–25°C). The mixture was evaporated *in vacuo*, and the residue was crystallized from ethanol. The diastereomers D_1 (less soluble) and D_2 of compound **6** were separated by several fractional crystallizations under TLC control (CH_2Cl_2/hexane = 2:1; vanilline and H_2SO_4; R_f (D_1) = 0.73, R_f (D_2) = 0.60).

(7R10R11R/7S10S11S)-7,11-Dibromo-8,8, 10-trimethyl-1,5-dioxaspiro[5.5]undecane (**2**; $C_{12}H_{20}Br_2O_2$)

Yield: 65%; while crystals; m.p.:85–86°C; ^{1}H NMR (C_6D_6, δ, 400 MHz): 0.51 (m (overlapped peaks), 1H, 3-H$_{eq}$), 0.87 (d, 3H, J = 6.5 Hz, 10-CH$_3$(eq)), 1.00 (s, 3H, 8-CH$_3$(eq)), 1.09 (m

(overlapped peaks), 1H, 9-H_{eq}), 1.21 (s, 3H, 8-CH_3(*ax*)), 1.58 (t (overlapped dd), 1H, $J = J' = 13.2$ Hz, 9-H_{ax}), 1.68-1.85 (m (overlapped signals), 2H, 3-H_{ax}, 10-H_{ax}), 306 (dt (overlapped ddd), 1H, $J = J' = 11.8$, $J'' = 2.8$ Hz, 2-H_{ax}), 3.36 (ddt (overlapped dddd), 1H, $J = 11.8$, $J' = 5.5$, $J'' = J''' = 1.7$ Hz, 2-H_{eq}), 3.41 (dt (overlapped ddd), 1H, $J = J' = 11.8$, $J'' = 2.7$ Hz, 4-H_{ax}), 3.53 (ddt (overlapped dddd), 1H, $J = 11.8$, $J' = 5.5$, $J'' = J''' = 1.7$ Hz, 4-H_{eq})[1], 4.46 (s, 1H, 7-H_{ax}), 4.53 (t (overlapped dd), 1H, $J = J' = 2.3$ Hz, 11-H_{eq}) ppm; ^{13}C NMR (C_6D_6, δ, 100 MHz): 20.70 (10-CH_3(eq)), 23.72 (8-CH_3(eq)), 24.06 (C^3), 28.96 (8-CH_3(ax)), 32.02 (C^{10}), 37.29 (C^8), 42.94 (C^9), 58.63 (C^2), 59.16 (C^{11}), 59.86 (C^4), 67.24 (C^7), 97.55 (C^6) ppm.

(7R10R11R/7S10S11S)-7,11-Dibromo-3,3,8,8,10-pentamethyl-1,5-dioxaspiro[5.5]undecane (**4**; $C_{14}H_{24}Br_2O_2$)

Yield: 70%; white crystals; m.p.: 92–94°C, ^{1}H NMR (C_6D_6, δ, 400 MHz): 0.20 (s, 3H, 3-CH_3(*eq*)), 0.87 (d, 3H, $J = 6.5$ Hz, 10-CH_3(*eq*)), 1.01 (s, 3H, 8-CH_3(*eq*)), 1.10 (m (overlapped peaks), 1H, 9-H_{eq}), 1.23 (s, 3H, 8-CH_3(*ax*)), 1.31 (s, 3H, 3-CH_3(*ax*)), 1.60 (t (overlapped dd), 1H, $J = J' = 13.0$ Hz, 9-H_{ax}), 1.81 (m (overlapped peaks), 1H, 10-H_{ax}), 3.05 (d, 1H, $J = 11.5$ Hz, 2-H $_{ax}$), 3.11 (dd, 1H, $J = 11.8$, $J' = 2.2$ Hz, 2-H_{eq})[1], 3.24 (dd, 1H, $J = 11.5$, $J' = 2.2$ Hz, 4-H_{eq})[1], 3.40 (d, 1H, $J = 11.5$ Hz, 4-H_{ax}), 4.57 (s, 1H, 7-H_{ax}), 4.73 (t (overlapped dd), 1H, $J = J' = 2.2$ Hz, 11-H_{eq}) ppm; ^{13}C NMR (C_6D_6, δ, 100 MHz): 20.73 (10-CH_3(eq)), 21.84 (3-CH_3(eq)), 23.46 (3-CH_3(*ax*)), 23.74 (8-CH_3(eq)), 28.99 (8-CH_3(*ax*)), 32.90 (C^{10}), 37.05 (C^3), 37.28 (C^8), 43.06 (C^9), 58.05 (C^{11}), 66.67 (C^7), 69.25 (C^2), 70.44 (C^4), 97.84 (C^6) ppm.

7,11, Dibromo-2,8,8,10-tetramethyl-1,5-dioxaspiro[5.5]undecane (**6**; $C_{13}H_{22}Br_2O_2$)
Yield: 65%; white crystals.

D$_1$ (2*R*, 7*R*, 10*R*, 11*R*/2*S*, 7*S*, 10*S*, 11*S*): M.p.: 149–150°C; ^{1}H NMR (C_6D_6, δ, 400 MHz): 0.65 (m (overlapped peaks), 1H, 3-H_{eq}), 0.91 and 0.92 (two overlaped doublets, 6H, $J = 6.3$ Hz, 2-CH_3(*eq*), 10-CH_3(*eq*)), 1.03 (s, 3H, 8-CH_3(*eq*)), 1.15 (m (overlapped peaks), 1H, 9-H_{eq}), 1.24 (s, 3H, 8-CH_3(*ax*)), 1.44 (dq (overlapped dddd), 1H, $J = J' = J'' = 12.5$, $J''' = 5.2$ Hz, 3-H_{ax}), 1.62 (t (overlapped dd), 1H, $J = J' = 13.2$ Hz, 9-H_{ax}), 1.85 (m (overlapped peaks), 1H, 10-H_{ax}), 3.15 (doublet of sextets (overlapped ddg), 1H, $J = 11.8$, $J' = 6.0$, $J'' = 2.7$ Hz, 2-H_{ax}), 3.42 (dt (overlapped ddd), 1H, $J = J' = 12.0$, $J'' = 2.3$ Hz, 4-H_{ax}), 3.58 (ddd, 1H, $J = 12.0$, $J' = 5.2$, $J'' = 1.5$ Hz, 4-H_{eq}), 4.49 (s, 1H, 7-H_{ax}), 4.57 (t (overlapped dd), 1H, $J = J' = 2.2$ Hz, 11-H_{eq}) ppm; ^{13}C NMR (C_6D_6, δ, 100 MHz): 20.84 (10-CH_3(*eq*)), 22.05 (2-CH_3(*eq*)), 23.69(8-CH_3(*eq*)), 29.08 (8-CH_3(*ax*)), 31.53 (C^3), 33.04 (C^{10}), 37.31 (C^8), 42.98 (C^9), 58.96 (C^{11}), 59.40 (C^7), 65.63 (C^4), 67.13 (C^2), 97.95 (C^6) ppm.

D$_2$ (2*S*,7*R*,10*R*,11*R*,/2*R*,7*S*,10*S*,11*S*): M.p.: 134–136°C; ^{1}H NMR (C_6D_6, δ, 400 MHz): 0.67 (m (overlapped peaks), 1H, 3-H_{eq}), 0.88 (d, 3H, $J = 6.0$ Hz, 10-CH_3(*eq*)), 1.01 (s, 3H, 8-CH_3(*eq*)), 1.08 (d, 3H, $J = 6.0$ Hz, 2-CH_3(*eq*)), 1.09 (m (overlapped peaks), 1H, 9-H_{eq}), 1.23 (s, 3H, 8-CH_3(*ax*)), 1.46 (dq (overlapped dddd), 1H, $J = J' = J'' = 12.5$, $J''' = 5.2$ Hz, 3-H_{ax}), 1.60 (t (overlapped dd), 1H, $J = J' = 12.7$ Hz, 9-H_{ax}), 1.82 (m (overlapped peaks), 1H, 10-H_{ax}), 3.08 (dt overlapped ddd), 1H, $J = J' = 12.0$, $J'' = 2.7$ Hz, 4-H_{ax}), 3.43 (ddd, 1H, $J = 12.0$, $J' = 5.2$, $J'' = 1.6$ Hz, 4-H_{eq}), 3.45 (doublet of sextets (overlapped ddq), 1H, $J = 12.0$, $J' = 5.8$, $J'' = 2.7$ Hz, 2-H_{ax}), 4.46 (s, 1H, 7-H_{ax}), 4.50 (t (overlapped dd), 1H, $J = J' = 2.4$ Hz, 11-H_{eq}) ppm; ^{13}C NMR (C_6D_6, δ, 100 MHz): 20.81 (10-CH_3(*eq*)), 21.93 (2-CH_3(*eq*)), 23.73 (8-CH_3(*eq*)), 29.07 (8-CH_3(*ax*)), 31.44 (C^3), 33.01 (C^{10}), 37.29 (C^8), 42.93 (C^9), 59.78 (C^{11}), 60.23 (C^7), 64.73 (C^4), 67.36 (C^2), 98.00 (C^6) ppm.

[1] Further splitting is due to long-range coupling of 2*e* with 4*e* (W arrangement of H_{eq}-C(2)-C(3)-C(4)-H_{eq})

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