A New Rotane Family: Synthesis, Structure, Conformation, and Dynamics of [3.4]-, [4.4]-, [5.4]-, and [6.4]Rotane[1]

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Abstract: The synthesis, structure, conformation, and dynamics of a new rotane family consisting of four-membered rings are described. All syntheses are based on bicyclobutylidene (**9**): [2+1] cycloaddition of cyclobutylidene yields [3.4]rotane (**5**) (**9**−**5**), [2+2] cycloaddition of trimethyleneketene followed by spiroalkylation of the resulting trispiroketone **10** yields [4.4]rotane (**6**) (**9**−**10**−**13**−**14**−**6**), homologization of **10** via *β*-hydroxy selenides gives access to tetraspiroketone **11** and pentaspiroketone **12** (**10**−**15**−**11**−**16**−**12**), and further elaboration directed toward a cyclopropylcarbene−cyclobutene rearrangement yields [5.4]-rotane (**7**) and [6.4]rotane (**8**) [**11**(**12**)−**18**(**24**)−**19**(**25**)−**20**(**26**)−**21**(**27**)−**22**(**28**)−**23**(**29**)−**7**(**8**)]. The structures of **6**, **7**, and **8** were determined by high-precision low-temperature X-ray analyses and by force field calculations using the search routine HUNTER in connection with MM3(92). The following special features were observed: From **5** to **8**, the bond angles of the central ring increase while the bond angles at the spiro center of the spiroannelated cyclobutane rings decrease. As a consequence, the cyclobutane rings change their geometry from a regular trapezoid in **6** to a kite with the smallest angle at the spiro center in **7** and **8**. At the same time their folding decreases, until in **8** they are close to planar. At room temperature, all hexaspiranes (**8**, **25**−**29**) are conformationally stable. This phenomenon allowed a stereoselective synthesis of axially labeled [1-^{13}C]-**8'** and, via a high-temperature equilibration with equatorially labeled [1-^{13}C]**8**, a determination of the free energy of activation for the chair to chair interconversion as $\Delta G^{\ddagger}_{487} = 156.8 \pm 1.1$ kJ/mol. This is the highest barrier of inversion ever reported for a cyclohexane. Promising candidates for even higher barriers are [6.5]-rotane (**32**) and [6.6]rotane (**33**).

Introduction

[*m.n*]Rotanes are composed of an *m*-membered central ring ($m = 3, 4, 5, ...$) and *m n*-membered peripheral rings ($n = 3, 4, 5, ...$) such that each atom of the central ring is at the same time part of a peripheral ring.[2] Originally denominated as [*n*]-rotanes[3] and restricted to polyspiranes of three-membered rings, they have attracted considerable interest. Beginning with the synthesis of [5.3]rotane (**3**)[3] and [4.3]rotane (**2**)[4] in 1969, and followed by the synthesis of [3.3]rotane (**1**)[5] in 1973, the first rotane family was complete with the synthesis of [6.3]rotane (**4**)[6] in 1976 (Chart 1). [6.3]Rotane (**4**) was the first per(cyclo)-alkylated cyclohexane existing at room temperature in solution in a fixed chair conformation.[7] Its barrier of inversion ($G^{\neq}_{298}$ = 89.4 ± 1.0 kJ/mol)[6,7a] was the highest of a cyclohexane known at the time. During the years which followed, the physical−chemical properties[8] and structural parameters[9] of **1**−**4**

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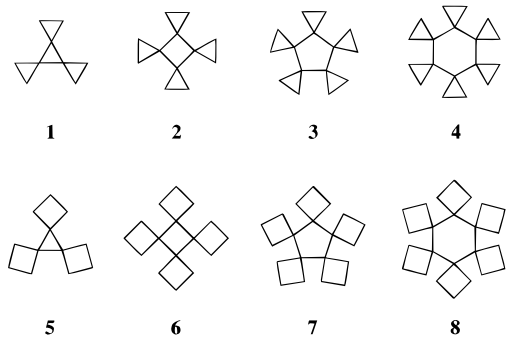
Chart 1



were studied, and incomplete rotanes derived from **4** were rearranged, yielding incomplete [6.4]coronanes.[10] Today, the chemistry of rotanes composed of three-membered rings is very well known, and papers on more elaborate structures containing spiroannelated three-membered rings ([*n*]triangulanes,[11] [*n*]-cyclotriangulanes,[11] "exploding" rotanes[12]) are beginning to appear.

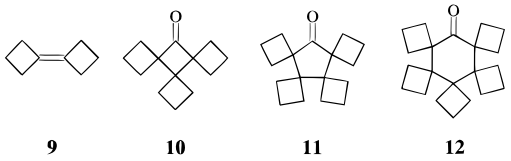
For several reasons **5**−**8** (Chart 1) and hence rotanes of four-membered rings are attractive synthetic goals: first, the complete lack of knowledge of how to construct, homologize, and spiroalkylate functionalized polyspiranes of four-membered rings, second, an early report[13] on an unsuccessful synthesis of [3.4]rotane (**5**), and third, the definitive expectation that [6.4]-rotane (**8**) would exhibit conformational isomerism[14] at room temperature and a barrier of inversion (160 kJ/mol)[7d] far beyond that of **4**. In the following, we give a full account of the synthesis, structure, conformation, and dynamics of the complete series **5**−**8**.

Results and Discussion

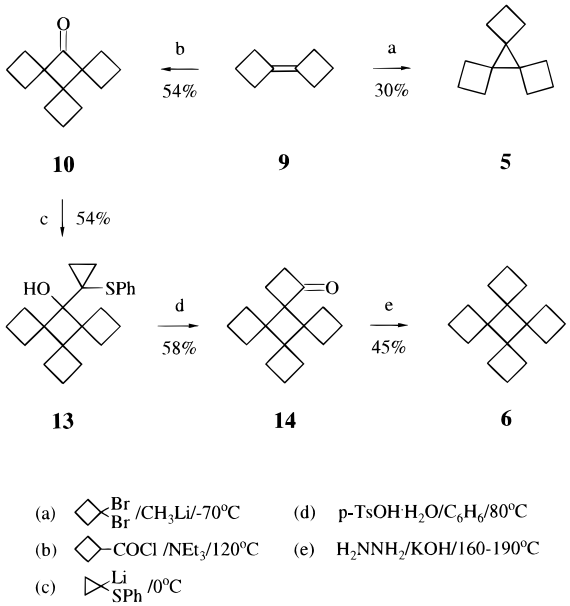
Our approach to **5**−**8** was based on the idea that the readily available bicyclobutylidene (**9**)[15] could open the way to all compounds desired: [2+1] cycloaddition of cyclobutylidene could deliver **5**, and [2+2] cycloaddition of trimethyleneketene followed by 2-fold homologization could lead to **10**−**12** (Chart 2) and, by subsequent spiroalkylation, to **6**−**8**.

Synthesis of [3.4]Rotane (5) and [4.4]Rotane (6). For the synthesis of [3.4]rotane (**5**) and [4.4]rotane (**6**) we envisaged an addition of cyclobutylidene to bicyclobutylidene (**9**) and a spiroalkylation of trispiroketone **10**, respectively. It has been

Chart 2



Scheme 1



reported[13] that cyclobutylidene, as generated from cyclobutanone tosyl hydrazone, does not add to bicyclobutylidene (**9**). We therefore adopted the protocol of Brinker[16] and generated the cyclobutylidene at −70 °C by slow addition of methyllithium to a solution of dibromocyclobutane[17] in ether. In the presence of an excess of bicyclobutylidene (**9**) we obtained the desired [3.4]rotane (**5**) (symmetry D_{3h}) in 30% yield, easily recognized by the appearance of only three resonances in the ^{13}C NMR spectrum [15.39 (d), 22.11 (d), 30.64 (s)].

For the synthesis of [4.4]rotane (**6**) we reacted trimethyl-eneketene[18] with bicyclobutylidene (**9**) and spiroalkylated the resulting trispiroketone **10** using the procedure of Trost.[19] (See Scheme 1.) For the experimental realization, cyclobutanecar-boxylic acid chloride (0.10 mol) was added to a solution of triethylamine (0.15 mol) in a large excess of bicyclobutylidene (**9**) (100 mL) and the resulting mixture heated for 5 h to 120 °C. After acidic workup, **10** (bp 76 °C/0.6 Torr; yield 54%) was isolated by distillation. Unchanged **9** (bp 145−148 °C)[15] could be recovered as the first fraction. At lower temperatures and with a less pronounced excess of bicyclobutylidene the yields were distinctly lower. To achieve the spiroalkylation, **10** was reacted with 1-lithiocyclopropyl phenyl sulfide[19a] and the resulting β-hydroxy sulfide **13** ring enlarged and hydrolyzed to cyclobutanone **14** by treatment with *p*-toluenesulfonic acid monohydrate in benzene.[19b] Wolff−Kishner reduction then

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(13) Bee, L. K.; Everett, J. W.; Garratt, P. J. *Tetrahedron* **1977**, *33*, 2143−2150.

(14) We use the term "conformational isomerism" in the sense defined by Dale (Dale, J. *Stereochemie und Konformationsanalyse*; Verlag Chemie: Weinheim, 1978). For this and other definitions, see also: Ernst, L. *Chem. Unserer Zeit* **1983**, *17*, 21.

(15) Fitjer, L.; Quabeck, U. *Synthesis* **1987**, 299−300.

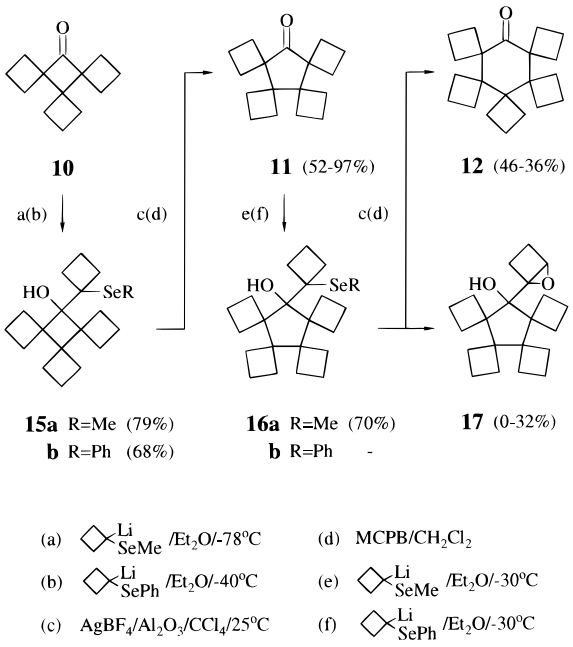
(16) Brinker, U. H.; Boxberger, M. *Angew. Chem.* **1984**, *96*, 971−972; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 974−975.

(17) Blankenship, C.; Paquette, L. A. *Synth. Commun.* **1984**, *14*, 983−987.

(18) Cycloadditions of trimethyleneketene to other compounds were not known. Its dimerization has been described: Erickson, J. L. E.; Collins, Jr., F. E.; Owen, B. L. *J. Org. Chem.* **1966**, *31*, 480−484.

(19) (a) Trost, B. M.; Keeley, D. E.; Arndt, H. C.; Rigby, J. H.; Bagdanowicz, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3080−3087. (b) Trost, B. M.; Keeley, D. E.; Arndt, H. C.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3088−3100.

Scheme 2



yielded [4.4]rotane (**6**) (effective symmetry D_{4h}), and once again the appearance of only three resonances in the ^{13}C NMR spectrum [16.58 (d), 25.20 (d), 50.19 (s)] indicated the final success.

Homologization of Trispiroketone 10. For the synthesis of [5.4]rotane (**7**) and [6.4]rotane (**8**) we needed the tetra- and pentaspiroketones **11** and **12**, respectively. We therefore explored the possibility of a ring enlargement of **10** via β-hydroxy selenides[20] using 1-lithio-1-(methylseleno)-[21] and 1-lithio-1-(phenylseleno)cyclobutane.[21] Indeed, both reagents added to trispiroketone **10** to give the desired β-hydroxy selenides **15a** and **15b**, respectively, which could be ring enlarged to tetraspiroketone **11** by treatment with silver tetrafluoroborate on aluminium oxide or 3-chloroperoxybenzoic acid. (See Scheme 2.)

Attempts to repeat the homologization with 1-lithio-1-(phenylseleno)cyclobutane failed. However, 1-lithio-1-(methylseleno)cyclobutane reacted smoothly, and ring enlargement of the resulting β-hydroxy selenide **16a** using silver tetrafluoroborate on aluminium oxide completed the synthesis of **12**.[22] With 3-chloroperoxybenzoic acid a considerable amount of epoxide **17** was formed. The successful homologization **10**−**11**−**12** represents a further example for the usefulness of selenium-stabilized carbanions for sterically demanding addition reactions otherwise difficult to achieve.[23]

Synthesis of [5.4]Rotane (7) and [6.4]Rotane (8). As already pointed out, the expected barrier of inversion of [6.4]-rotane (**8**) was so extremely high (160 kJ/mol)[7d] that an experimental determination through dynamic NMR could be excluded and the necessity to synthesize stereospecifically labeled material for a classical equilibration study became obvious. Clearly, the spiroalkylation used for the synthesis of [4.4]rotane (**6**) was unsuitable, but a synthesis via a cyclopropylcarbene−cyclobutene rearrangement[24] seemed promising. In this case, specific labeling with carbon-13 could be introduced in the first step, and specific labeling with deuterium in the first or the last step of a sequence beginning with a methylenation (**12**−**24**) and ending with a hydrogenation (**29**−**8**). All intermediates (**25**−**28**) were expected to be conformationally stable while the regiochemistry of the cyclopropylcarbene to cyclobutene rearrangement (**28**−**29**) was recognized as of no influence on the stereochemical result. (See Scheme 3.)

For the synthesis of unlabeled [5.4]rotane (**7**) and [6.4]rotane (**8**) the ketones **11** and **12** were subjected to high-temperature methylenations[25] and the products **18** and **24** converted by copper-catalyzed decomposition of methyl diazoacetate into the pentaspirane **19** (mp 65 °C), and the conformationally isomeric hexaspiranes **25** (mp 130−134 °C) and **25'** (mp 147−151 °C), respectively. The stereochemistry of the hexaspiranes was secured by an X-ray analysis of the minor isomer **25'**,[26] while the major isomer **28** was used for further elaboration. Reduction of **19** and **25** with lithium aluminium hydride afforded the alcohols **20** (mp 49 °C) and **26** (mp 135−185 °C), respectively, and Swern oxidation[27] yielded the aldehydes **21** and **27**, respectively. Reaction of **21** and **27** with tosyl hydrazide in dichloromethane/triethylamine[28] and heating of the resulting hydrazones **22** and **28** with sodium methoxide in diethylene glycol dimethyl ether yielded the cyclobutenes **23** (mp 105 °C) and **29** (mp 175−188 °C), respectively, which were hydrogenated over palladium on carbon in pentane to afford the desired [5.4]rotane (**7**) (mp 70−110 °C) and [6.4]rotane (**8**) (mp 274 °C), respectively. Deuteration of **29** yielded [1,2-D_2]**8**. As with **4** and **5**, the structures of the new rotanes followed from their ^{13}C NMR spectra. At room temperature, **7** [16.78 (d), 27.40 (d), 55.30 (s)] shows three resonances for a planar or rapidly inverting species (effective symmetry D_{5h}), while **8** [16.76 (d), 25.65 (d), 28.53 (d), 49.79 (s)] shows four resonances for a fixed chair conformation (symmetry D_{3d}).

Crystal Structures and Force Field Calculations. Suitable crystals for high-precision low-temperature X-ray analyses could be obtained from [4.4]rotane (**6**), [5.4]rotane (**7**), and [6.4]rotane (**8**). As several unusual structural features emerged, **6**−**8** were also subjected to force field calculations using the conforma-

(20) Ring expansions via β-hydroxy selenides are known: (a) Labar, D.; Krief, A. *J. Chem. Soc., Chem. Commun.* **1982**, 564−566. (b) Labar, D.; Laboureur, J. L.; Krief, A. *Tetrahedron Lett.* **1982**, *23*, 983−986. (c) Laboureur, J. L.; Krief, A. *Tetrahedron Lett.* **1984**, *25* 2713−2716. The insertion of a cyclobutane is new.

(21) Synthesis of selenoketals: (a) Krief, A.; Clarembeau, M.; Cravador, A.; Dumont, W.; Hevesi, L.; Luchetti, J.; van Ende, D. *Tetrahedron* **1985**, *41*, 4793−4812. Reductive metalations: (b) Krief, A. *Tetrahedron* **1980**, *36*, 2531−2640.

(22) For an alternative synthesis, see: (a) Fitjer, L.; Giersig, M.; Clegg, W.; Schormann, N.; Sheldrick, G. M. *Tetrahedron Lett*. **1983**, *24*, 5351−5354. (b) Giersig, M.; Wehle, D.; Fitjer, L.; Schormann, N.; Clegg, W. *Chem. Ber*. **1988**, *121*, 525−531.

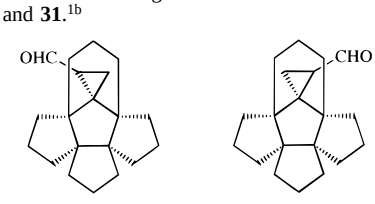
(23) 1-Lithiocyclobutyl phenyl sulfide and cyclopropylidene triphenylphosphorane did not react with **11**.

(24) Review: Shapiro, R. H. *Org. React. (N.Y.)* **1976**, *23*, 405−507.

(25) Fitjer, L.; Quabeck, U. *Synth. Commun.* **1985**, *15*, 855−864.

(26) The X-ray crystal structure data of **25'** are available as Supporting Information.

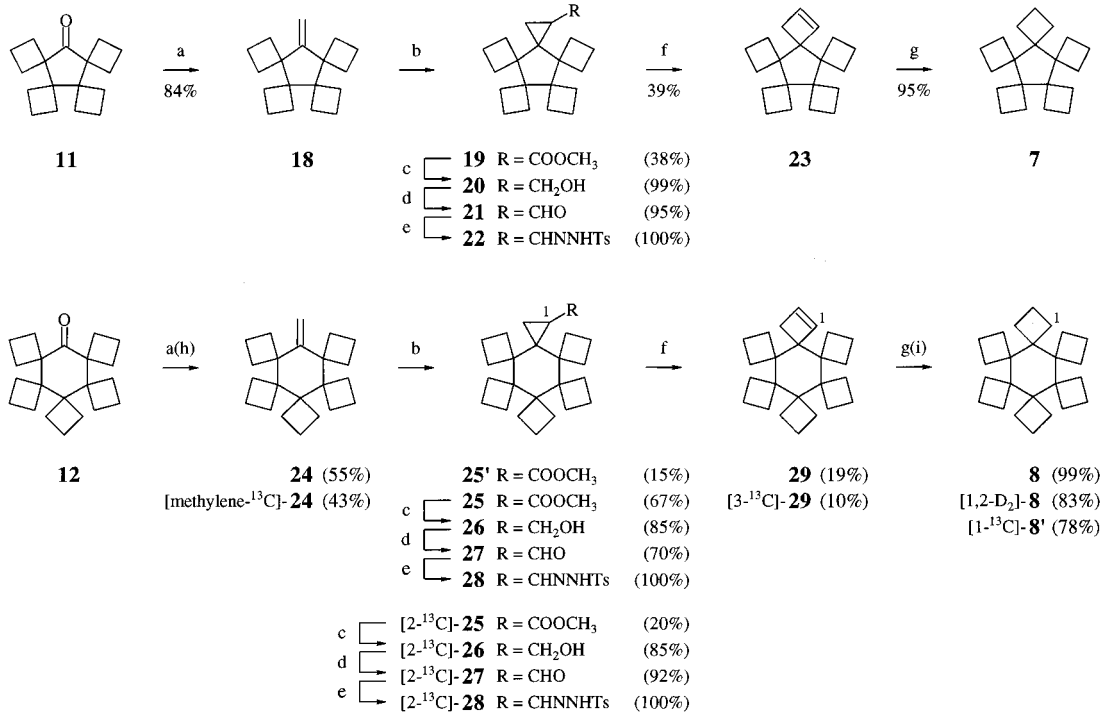
(27) Review: Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165−185. **21** and **27** were used as crude products and contained small amounts of triethylamine. Upon attempting a chromatographic purification on silica gel in dichloromethane **21** rearranged to a mixture of two stereoisomeric aldehydes, **30** and **31**.[1b]



30 **31**

(28) By treatment with tosyl hydrazide in aqueous methanol (Wiberg, K. B.; Lavanish, J. M. *J. Am. Chem. Soc.* **1966**, *88*, 5272−5275) **21** rearranged to a single tosylhydrazone derived from one of the two stereoisomeric aldehydes obtained during attempted chromatographic purification of **21**.

Scheme 3



(a) $Ph_3P{=}CH_2$, (b) $N_2CHCOOCH_3$/Cu, (c) $LiAlH_4$, (d) $(COCl)_2$/DMSO/NEt_3(e) $TsNHNH_2$/NET_3, (f) CH_3ONa, (g) H_2/Pd/C (h) $Ph_3{=}[^{13}C]H_2$, (i) D_2/Pd/C. In primed formulas C1 is in the axial position,in formulas without a prime C1 is equatorial.

Table 1. Averaged Values for Selected Bond Lengths, Bond Angles, and Puckering Angles in **6**−**8** As Determined by Force Field Calculations and by X-ray Analysis

rotane	*a* (Å)	*b* (Å)	*c* (Å)	α (deg)	*β* (deg)	*γ* (deg)	*δ* (deg)	*ϕ* (deg)	method
6	1.544	1.547	1.547	87.5	88.6	88.7	88.6	24.8	X-ray
	1.543	1.546	1.561	87.4	90.4	86.1	89.2	31.0	MM3
7	1.549	1.563	1.539	103.6	87.5	89.8	89.2	17.5	X-ray
	1.537	1.570	1.557	104.0	86.7	89.5	87.6	26.7	MM3
8	1.545	1.572	1.541	112.6	88.0	90.9	90.2	3.0	X-ray
	1.545	1.582	1.556	113.2	87.2	91.9	89.0	0.0	MM3

tional search routine HUNTER[29] in connection with MM3(92).[30] ORTEP plots of the X-ray crystal structures are given in Figure 1, and selected experimental and calculated structural data are collected in Table 1.

In the crystal state, the cyclobutane rings in [4.4]rotane (**6**) are systematically folded (ϕ = 33.4° (central ring) and 24.9 and 24.7° (peripheral rings)). In [5.4]rotane (**7**), the cyclopentane ring adopts a slightly distorted envelope conformation: C(1), C(5), C(9), and C(17) form an almost perfect plane (mean deviation 0.021 Å), while the flap atom C(13) is located 0.684 Å above this plane. The cyclobutane rings at C(13) and C(9) are nearly planar (ϕ = 9.7°) and planar (ϕ = 0.2°), respectively. The remaining three cyclobutane rings are moderately puckered (ϕ = 23.1, 26.5, and 28.2°). In [6.4]rotane (**8**), the cyclohexane ring adopts a slightly flattened chair conformation ($\sum|\theta|$ = 308.4°). All cyclobutane rings are close to planar (ϕ = 1.0, 3.8, and 4.2°), and all proximal cyclobutane bonds are perfectly staggered ($|\theta|$ = 48.6−50.0°).

Interesting anomalies are observed in the spiroannelated cyclobutane rings (Table 1): In **6**, the averaged lengths of the proximal and the distal bonds are identical ($b = c$ = 1.547 Å), but in **7** and **8**, the proximal bonds are elongated (b = 1.563 (**7**) and 1.572 (**8**) Å) and the distal bonds are shortened (c = 1.539 (**7**) and 1.541 (**8**) Å). A similar course follows for the corresponding bond angles β and δ: These angles are identical in **6** ($\beta = \delta$ = 88.6°), but in going to **7** and **8**, β decreases (β = 87.5° (**7**), and 88.0°) and δ increases (δ = 89.2° (**7**) and 90.2° (**8**)). Obviously, the increase in α (α = 87.5° (**6**), 103.6° (**7**), and 112.6° (**8**)) translates to a decrease in β and an increase in δ with concomitant lengthening of b and shortening of c. (See Chart 3.) As a result, the spiroannelated cyclobutane rings change their geometry from a regular trapezoid in **6** to a kite with the smallest angle at the spiro center in **7** and **8**. In [3.4]-rotane (**5**) the situation should be inverse.[31]

Due to a lack of parameters, [3.4]rotane (**5**) was not accepted by MM3(92). The parameters for all other rotanes were available. Within 3 kcal above the global minimum the search routine HUNTER located four conformers for **6**, five conformers for **7**, and a single conformer for **8**. All conformers of **6** and **8** and the four lowest in energy of **7** are shown in Figure 2.

In [4.4]rotane (**6**), the calculated global minimum conformation represents the conformation in the crystal state. In [5.4]-rotane (**7**), none of the four conformations lowest in energy

(29) Weiser, J.; Holthausen, M. C.; Fitjer, L. *J. Comput. Chem*. **1997**, *18*, 1264−1281. A Unix version of HUNTER connected with MM3(92) (QCPE #674) may be obtained from the Quantum Chemistry Program Exchange (QCPE), University of Indiana, Bloomington, IN 47405.

(30) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc*. **1989**, *111*, 8551−8556.

(31) For an experimental study on the closely related [3.3]rotane (**1**), see ref 9c.

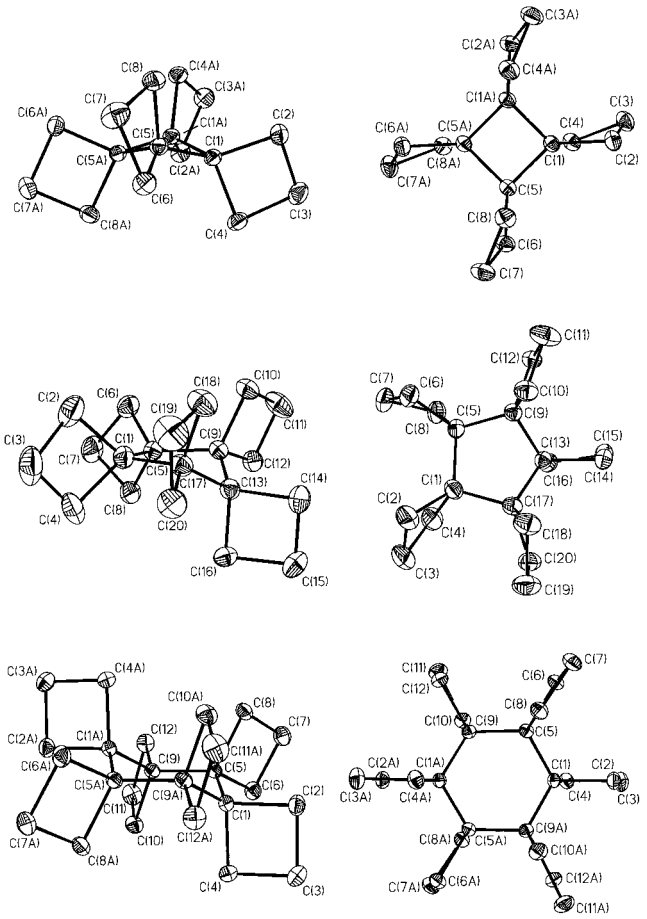


Figure 1. ORTEP plots of the X-ray crystal structures of **6**, **7**, and **8** (50% probability ellipsoids, hydrogen atoms omitted) in side view and top view.

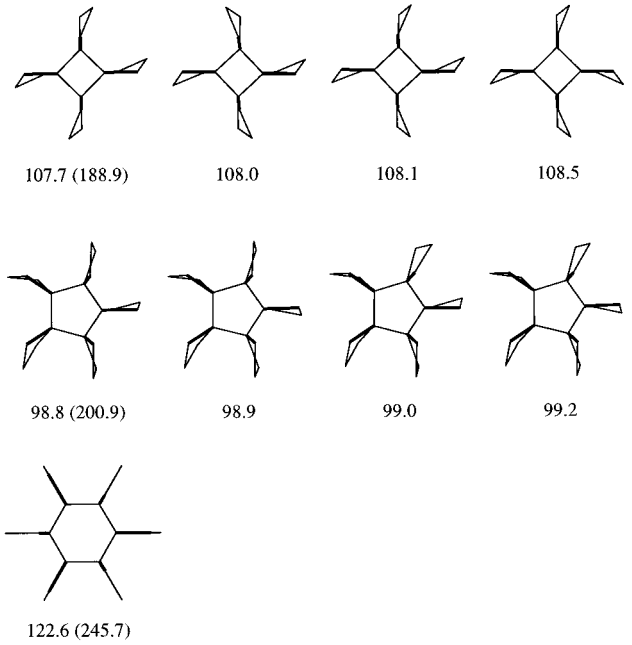
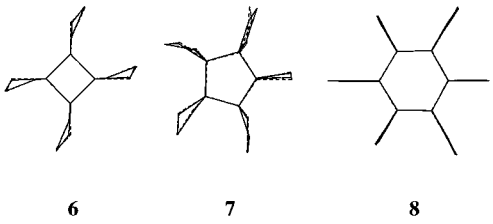


Figure 2. Low-energy conformations and corresponding heats of formation (strain energies) (kcal/mol) of **6**, **7**, and **8** as determined with HUNTER in connection with MM3(92).

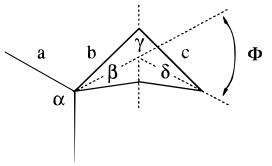
matches the crystal structure exactly. However, the global minimum conformation fits best: Four of the five cyclobutane rings are folded as in the crystal, and only one cyclobutane ring



6 **7** **8**

Figure 3. Least-squares fit of the X-ray crystal structures (continuous) and the calculated global minimum structures (dotted) of **6**, **7**, and **8**.

Chart 3



is planar in the crystal, but folded according to MM3(92). Interestingly, this cyclobutane ring is the only one where the anisotropic displacement parameters of the peripheral carbon atom (C(11)) even at −140 °C are large. In contrast to **6** and **7**, only a single low-energy conformer exists for [6.4]rotane (**8**). The geometry of this conformer is governed by strong nonbonding interactions and matches the crystal structure closely. A least-squares fit of the X-ray crystal structures and the calculated global minimum structures of **6**, **7**, and **8** is shown in Figure 3. In all cases, the mean deviations are small (**6**, 0.0632 Å; **7**, 0.0957 Å; **8**, 0.0395 Å). This indicates that MM3-(92) delivers reliable results.

Dynamics of [6.4]Rotane (8). [6.4]Rotane (**8**) is very sparingly soluble, and all attempts to determine its inversion barrier ^{2}H NMR spectroscopically via a high temperature equilibration of [1,2-D_2]**8** failed because of the large line widths and the poor solubility. To increase the sensitivity toward an NMR analysis, stereospecifically ^{13}C-labeled material had to be prepared. Therefore, **12** was methylenated with ([^{13}C]-methylene)triphenylphosphorane and subsequently converted to [1-^{13}C]**8'** as described for unlabeled **8** ([*methylene*-^{13}C]-**24** → [2-^{13}C]**25** → [2-^{13}C]**26** → [2-^{13}C]**27** → [2-^{13}C]**28** → [3-^{13}C]**29** → [1-^{13}C]**8'**).

Preliminary measurements revealed that the equilibration of [1-^{13}C]**8'** could best be followed by ^{13}C NMR spectroscopy (125.9 MHz, 1,3-bis([D_3]methoxy)benzene) at 214 °C using the resonances of the axial (26.01) and equatorial carbon atoms (28.82) of the cyclobutane rings. For the kinetic analysis, the spectra were taken at appropriate times and the intensities of the resonances of the axial (*I'*) and equatorial (*I*) carbon atoms measured by careful integration (Figure 4). As could have been expected, the equilibration followed first-order kinetics (Figure 5) and led to k([1-^{13}C]**8'**) = k([1-^{13}C]**8**) = (1.547 ± 0.019) × 10^{-4} s^{-1} at 214 ± 3 °C. Insertion of these data into the Eyring equation yielded the free energy of activation as $\Delta G^{\ddagger}_{487}$ = 156.8 ± 1.1 kJ/mol and thereby the highest barrier of inversion ever reported for a cyclohexane.

In view of the unusual properties of [6.4]rotane (**8**) it is tempting to speculate that cyclohexanes with even more pronounced anomalies could exist. In a search for possible candidates, we performed MM3 calculations on [6.5]rotane (**32**) and [6.6]rotane (**33**). Within 3 kcal above the global minimum the search routine HUNTER located more than 40 minima for **32** and more than 100 minima for **33**. In all cases, the central ring adopts a chair, while the peripheral rings exist in a large number of different combinations of envelope conformations in **32** and chair and/or boat conformations in **33**. Surprisingly, none of the high-symmetry conformations **32b** and **33b**−**d**,

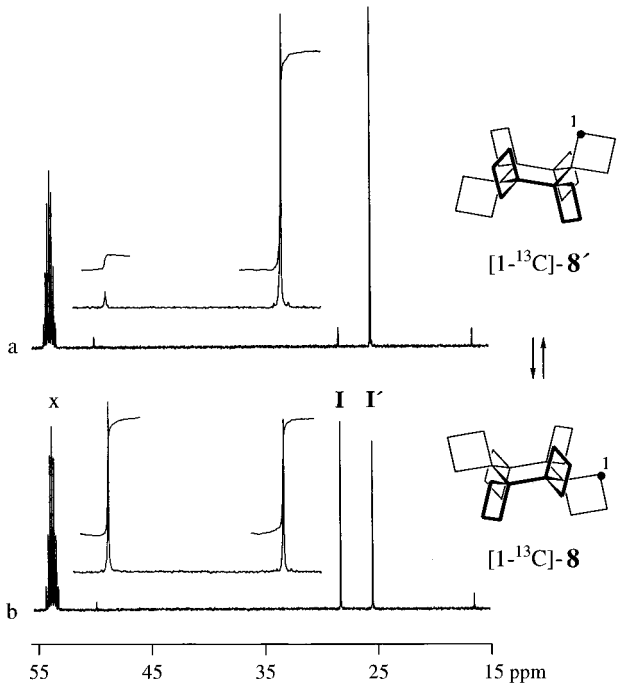


Figure 4. ^{13}C NMR spectra (125.9 MHz, 1,3-bis([D$_3$]methoxy)benzene (x), 50 °C) of [1-^{13}C]**8'**: (a) before and (b) after equilibration. Spectral parameters and details concerning the kinetic analysis are given in the Experimental Section.

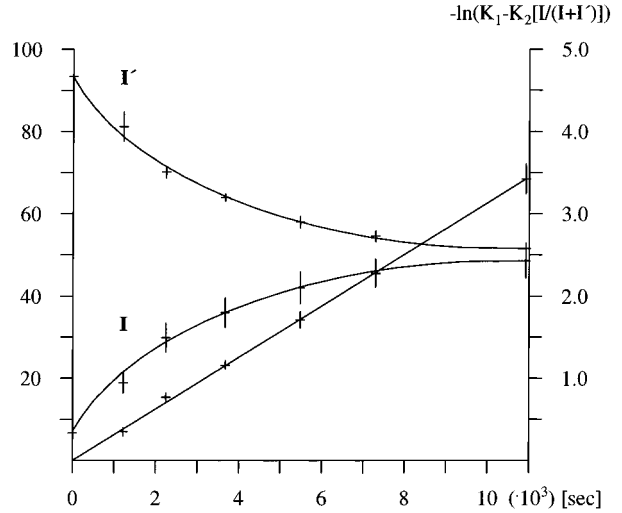


Figure 5. Time course of the intensity of the resonance lines for the axial (*I'*) and equatorial (*I*) carbon atoms of the cyclobutane rings in [1-^{13}C]**8'** at 214 °C, and least-squares approximation of $-\ln(K_1 - K_2[I/(I + I')]) = [k([1\text{-}^{13}\text{C}]\mathbf{8'}) + k([1\text{-}^{13}\text{C}]\mathbf{8})]t$ with $K_1 = 1 + 12p/(m - p)$ and $K_2 = 2(11p + m)/(m - p)$. The rate law includes corrections for the observed superposition of the resonance lines for magnetically equivalent labeled ($m = 99$) and unlabeled ($p = 1$) positions. Details are given in the Experimental Section.

respectively, represent a global minimum. According to MM3-(92), the global minima are the low-symmetry conformations **32a** and **33a** (Figure 6).

Clearly, the conformation and dynamics of [6.4]rotane (**8**), [6.5]rotane (**32**), and [6.6]rotane (**33**) must be governed by strong nonbonding interactions. A rough estimate for such interactions results if the calculated total strain energies (245.7 (**8**), 135.2 (**32**), 182.1 (**33**) kcal/mol) are reduced by the sum of the calculated strain energies of all individual rings (26.2 (cyclobutane), 7.1 (cyclopentane), 1.7 (cyclohexane) kcal/mol). The values obtained indicate that the nonbonding interactions

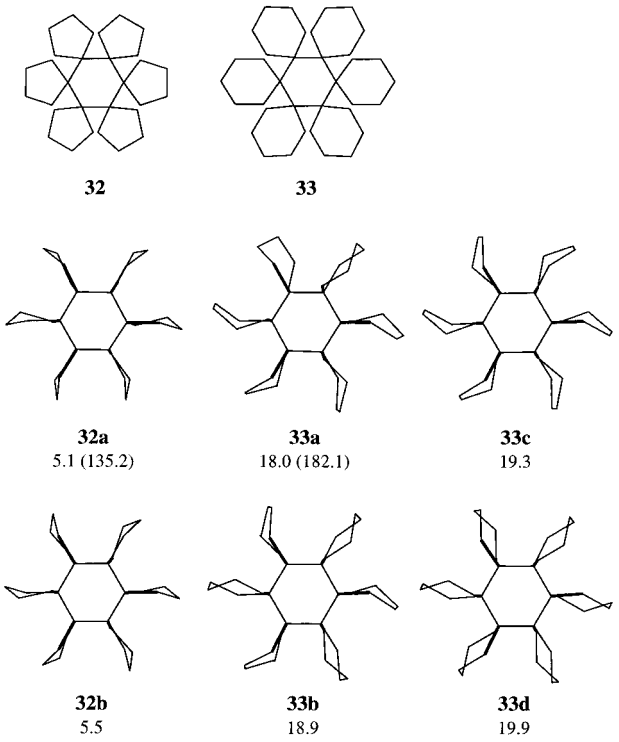


Figure 6. Selected low-energy conformations and corresponding heats of formation (strain energies) (kcal/mol) of **32** and **33** as determined with HUNTER in connection with MM3(92).

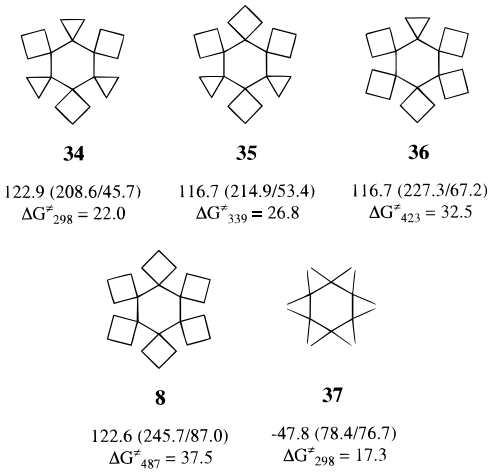


Figure 7. Heats of formation (strain energies/reduced strain energies) of **34**−**37** and **8** as determined with HUNTER in connection with MM3-(92), and experimental free energies of activation for the chair-to-chair interconversions (kcal/mol).

in **8** (87.0 kcal/mol) and **32** (90.9 kcal/mol) are indeed strong, but only half as strong as in **33** (170.3 kcal/mol). We therefore believe that a synthesis and investigation of the structure, conformation, and dynamics of the unknown rotanes **32** and **33** could lead to new frontiers.

A last note concerns the origin of the extraordinary barrier of [6.4]rotane (**8**) and its relation to the barriers of the hexaspiranes **34**,[7a] **35**[7c], and **36**,[7c] and the topologically simpler permethylcyclohexane (**37**)[32] (Figure 7). In the ground state, all compounds adopt a chair and the reduced strain energy, quantifying the nonbonding interactions and calculated as before, first strongly increases (45.7 (**34**), 53.4 (**35**), 67.2 (**36**), 87.0

(32) (a) Fitjer, L.; Scheuermann, H.-J.; Wehle, D. *Tetrahedron Lett.* **1984**, *25*, 2329−2332. (b) Wehle, D.; Scheuermann, H.-J.; Fitjer, L. *Chem. Ber.* **1986**, *119*, 3127−3140.

(**8**) kcal/mol), and then slightly decreases (76.7 kcal/mol (**37**)). In the transition state, the additional strain, quantified by the experimental free energies of activation,[33] first strongly increases (22.0 (**34**), 26.8 (**35**), 32.5 (**36**), 37.5 (**8**) kcal/mol), and then sharply decreases (17.3 kcal/mol (**37**)). Given the fact that cyclopropanes and cyclobutanes, as compared to a geminal dimethyl group, are well defined structural entities with a restricted motional freedom, the pronounced energetical response of the hexaspiranes **34**, **35**, **36**, and **8** to the inevitable approach of parts of the molecule during inversion was to be expected. However, a detailed analysis must await for a study of the conformational energy surface of all molecules in question. Such a study already exists for **37**.[34]

Summary and Conclusions

We report on the synthesis, structure, conformation, and dynamics of a new rotane family consisting of four-membered rings. The most important features of the synthetic part are a [2+1] cycloaddition of cyclobutylidene to bicyclobutylidene for the synthesis of [3.4]rotane (**5**) (**9**−**5**), a [2+2] cycloaddition of trimethyleneketene to bicyclobutylidene with subsequent spiroalkylation of the resulting trispiroketone **10** for the synthesis of [4.4]rotane (**6**) (**9**−**10**−**13**−**14**−**6**), a ring enlargement of **10** via β-hydroxy selenides for the synthesis of tetraspiroketone **11** and pentaspiroketone **12** (**10**−**15**−**11**−**16**−**12**), and a further elaboration directed to a cyclopropylcarbene−cyclobutene rearrangement for the synthesis of [5.4]rotane **(7**) and [6.4]rotane (**8**) [**11**(**12**)−**18**(**24**)−**19**(**25**)−**20**(**26**)−**21**(**27**)−**22**(**28**)−**23**(**29**)−**7**(**8**)].

The structures of **6**, **7**, and **8** were determined by high-precision low temperature X-ray analyses and by force field calculations using the search routine HUNTER in connection with MM3(92). The following special features were observed: From **5** to **8**, the bond angles within the central ring increase while the bond angles at the spiro center of the peripheral cyclobutane rings decrease. As a consequence, the peripheral cyclobutane rings change their geometry from a regular trapezoid in **6** to a kite with the smallest angle at the spiro center in **7** and **8**. At the same time, the cyclobutane rings become less folded, until in [6.4]rotane (**8**) they are nearly planar. This documents increasingly strong nonbonding interactions, leading to an extremely well-defined ground state geometry in **8**.

The most important result concerns the dynamics of [6.4]-rotane (**8**). All hexaspiranes (**8**, **25**−**29**) exist at room temperature in a fixed chair conformation and preserve their stereochemistry through sufficiently high barriers of inversion. For the determination of the inversion barrier of **8**, we synthesized axially labeled [1-^{13}C]**8'** and followed its equilibration with equatorially labeled [1-^{13}C]**8** by ^{13}C NMR spectroscopy at 214 °C. The equilibration followed first-order kinetics and yielded the free energy of activation for the chair to chair interconversion as $\Delta G^{\ddagger}_{487} = 156.8 \pm 1.1$ kJ/mol. This is the highest barrier of inversion ever reported for a cyclohexane. Promising candidates for even higher barriers are [6.5]rotane (**32**) and [6.6]rotane (**33**).

Experimental Section

IR spectra were recorded on a Perkin-Elmer 298 or a Bruker IFS 25 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with a Varian EM 360, FT 80 A, AH 100, XL 200, VXR 200, or VXR 500 or a Bruker AMX 300 spectrometer. For standards other than TMS the following chemical shifts were used: $\delta_H(CHDCl_2) = 5.32$ ppm, $\delta_H(CHCl_3) = 7.24$ ppm, $\delta_H(C_6HD_5) = 7.28$ ppm, $\delta_C(CD_2Cl_2) = 53.80$ ppm, $\delta_C(CDCl_3) = 77.00$ ppm, $\delta_C(C_6D_6) = 128.00$ ppm, and δ_C[1,3-$(CD_3O)_2C_6H_4$, hept] = 54.05 ppm. Some of the ^{13}C NMR spectra were studied by APT (attached proton test) to determine the number of protons attached to each carbon. Mass spectra were determined with a Varian MAT 311 A, Varian MAT 731, or a Finnigan MAT 95 instrument operated at 70 eV. Preparative GC was carried out on an Intersmat IGC 16, Carlo Erba FTV 2450, or Delsi IGC 121 MLR instrument employing a thermal conductivity detector and hydrogen as the carrier gas. Product ratios were not corrected for relative response. R_f values are quoted for Macherey & Nagel Polygram SIL G/UV254 plates. Colorless substances were detected by oxidation with 3.5% alcoholic molybdophosphoric acid (Merck) and subsequent warming. Melting points were observed on a Reichert microhotstage or a Büchi melting point apparatus and are not corrected. Microanalytical determinations were done at the Microanalytical Laboratory of the Institute of Organic Chemistry, Göttingen.

Trispiro[3.0.3.0.3.0]dodecane ([3.4]Rotane) (5). To a stirred solution of 1,1-dibromocyclobutane[17] (10.7 g, purity 94%, 50 mmol) and bicyclobutylidene (**9**)[15] (21.6 g, 200 mmol) in anhydrous ether (50 mL) under nitrogen at −70 °C was added over a period of 20 min a 1.1 M solution of methyllithium in ether (68 mL, 75 mmol). Stirring was continued at −70 °C until GC analysis [3 m × 1/4 in. all glass system, 15% OV 210 on Chromosorb W AW/DMCS 60−80 mesh, 100 °C; relative retention times: 1.00 (**9**), 2.82 (1,1-dibromocyclobutane), 4.08 (**5**)] indicated that 1,1-dibromocyclobutane had been consumed (1.5 h). The mixture was warmed to 0 °C over a period of 3 h hydrolyzed with water (50 mL), the layers were separated, the aqueous phase was extracted with ether (3 × 20 mL), and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated (bath temperature 30 °C, 15 Torr) and the yellow, liquid residue (23.4 g) chromatographed on silica gel (0.05−0.20 mm) in pentane [column 50 × 6 cm; R_f = 0.65 (**5**), 0.55 (**9**)], yielding 2.40 g (30%) of **5** as a colorless liquid: ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int) 1.66−1.76 (m, 12), 1.86−2.20 (m, 6); ^{13}C NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int) 15.35 (t), 22.11 (t), 30.64 (s); MS *m/z* 162 (2, M^+), 91 (100). Anal. Calcd for $C_{12}H_{18}$: C, 88.89; H, 11.11. Found: C, 88.91; H, 11.08.

Trispiro[3.0.3.0.3.1]tridecan-13-one (10). To a stirred solution of anhydrous triethylamine (15.2 g, 150 mmol) in bicyclobutylidene (**9**)[15] (100 mL, 87.8 g, 812 mmol) under nitrogen at 80 °C was added cyclobutanecarboxylic acid chloride (11.9 g, 100 mmol) and the resulting mixture heated for 5 h to 120 °C. After dilution with ether (200 mL) the salts were dissolved in water (20 mL), and the organic phase was washed with 2 N HCl (20 mL) and a saturated solution of sodium bicarbonate (20 mL) and dried ($MgSO_4$). Distillation over a 20 cm Vigreux column yielded first ether, then unchanged bicyclobutylidene (**9**) (70.8 g, bp 51 °C, 12 Torr), then dispiro[3.1.3.1]decan-5,10-one[18] (1.3 g, bp 70 °C, 2 Torr; mp 84−86 °C), and finally **10** as a colorless oil (10.3 g, 54%, bp 75−85 °C, 1 Torr): IR (neat) (C=O) 1760 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$, $CHCl_3$ int) 1.5−2.2 (m); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 15.54, 15.78, 23.80, 25.58, 44.80, 64.34, 216.01; MS *m/z* 190 (5, M^+), 80 (100). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.85; H, 9.45.

13-[1'-(Phenylsulfanyl)cyclopropyl]trispiro[3.0.3.0.3.1]tridecan-13-ol (13). To a stirred solution of cyclopropyl phenyl sulfide[19a] (3.16 g, 21.0 mmol) in anhydrous tetrahydrofuran (50 mL) under nitrogen at 0 °C was added within 15 min a 1.48 M solution of *n*-butyllithium in hexane (14.2 mL, 21.0 mmol). After 1 h at 0 °C, **10** (4.00 g, 21.0 mmol) was added within 15 min and the mixture stirred at 0 °C until TLC [pentane/ether, 9:1; R_f = 0.92, 0.53 (**10**), 0.48 (**13**), 0.25] indicated that **10** had been consumed (1.5 h). The mixture was diluted with ether (50 mL), washed with brine (25 mL), and dried ($MgSO_4$). The solvents were evaporated (bath temperature 50 °C, 12 Torr), and the red to yellow, liquid residue (7.00 g) was chromatographed on silica gel (0.05−0.20 mm) in pentane/ether (9:1; column 120 × 4 cm), yielding 3.84 g (54%) of **13** as a colorless solid: mp 67 °C; IR (neat) (O−H_{ass}) 3600−3200 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int) 0.91−0.99 (AA'-part of an AA'BB' system, 2), 1.25−1.33 (BB'-part of an AA'BB' system, 2), 1.72−2.05 (m, 10), 2.11−2.35 (m, 9), 7.13−

(33) Enthalpies of activation only exist for **34** ($\Delta H^{\ddagger}$ = 21.1 kcal/mol)[7a] and **37** ($\Delta H^{\ddagger}$ = 15.6 kcal/mol).[32]

(34) Ermer, O.; Ivanov, P. M.; Osawa, E. *J. Comput. Chem.* **1985**, *6*, 401−428.

7.21 (m, 3), 7.49−7.57 (m, 2); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int) 14.52 (t), 15.74 (t), 16.58 (t), 25.81 (t), 26.25 (t), 26.80 (t), 26.83 (t), 33.14 (s), 50.77 (s), 53.26 (s), 78.90 (s), 125.71 (d), 128.57 (d), 129.17 (d), 137.24 (s); MS *m/z* 340 (10, M^+), 232 (100). Anal. Calcd for $C_{22}H_{28}OS$: C, 77.60; H, 8.29; S, 9.42. Found: C, 77.57; H, 8.38; S, 9.47.

Tetraspiro[3.0.3.0.3.0.3.0]hexadecan-1-one (14). Benzene (60 mL) was saturated with water, **13** (3.84 g, 11.3 mmol) and *p*-toluenesulfonic acid monohydrate (1.95 g, 11.3 mmol) were added, and the mixture was heated to reflux until TLC [pentane/ether, 95:5; R_f = 0.47 (**13**), 0.38 (**14**)] indicated that **13** had been consumed (1.5 h). The mixture was washed with water (10 mL), saturated sodium bicarbonate (30 mL), and brine (30 mL) and dried ($MgSO_4$). The solvent was evaporated (bath temperature 25 °C, 15 Torr) and the red, liquid residue (3.11 g) chromatographed on silica gel (0.05−0.20 mm) in pentane/ether (95:5; column 70 × 4 cm), yielding 1.52 g (58%) of **42** as a colorless solid: mp 76 °C; IR (KBr) (C═O) 1770 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int) 1.63−2.07 (m, 20), 2.78 (t, 2, J = 8.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int) 15.93 (t), 16.16 (t), 16.73 (t), 24.11 (t), 24.54 (t), 26.18 (t), 26.34 (t), 43.77 (t), 49.92 (s), 50.51 (s), 75.34 (s), 212.20 (s); MS *m/z* 230 (1, M^+), 131 (100). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.14; H, 9.47.

Tetraspiro[3.0.3.0.3.0.3.0]hexadecane ([4.4]Rotane) (6). A stirred solution of 80% aqueous hydrazine hydrate (1.13 g, 18.0 mmol), grinded potassium hydroxide (1.35 g, 24.0 mmol), and **14** (1.38 g, 6.0 mmol) in diethylene glycol (12 mL) under nitrogen was heated to 160 °C until TLC [pentane/ether, 95:5; R_f = 0.95 (**6**), 0.38 (**14**), 0.04, 0.00 (hydrazone)] indicated that **14** had been consumed (2 h). The temperature was raised to 195 °C, a vigorous gas evolution occurred, and after 2 h at 195 °C the reaction was complete. The mixture was diluted with water (12 mL) and extracted with pentane (5 × 25 mL). The combined extracts were washed with water (3 × 30 mL), dried ($MgSO_4$), and concentrated on a rotary evaporator (bath temperature 25 °C, 12 Torr). Chromatography of the oily residue (886 mg) on silica gel (0.05−0.20 mm) in pentane (column 30 × 3 cm; R_f = 0.75) yielded 581 mg (45%) of **6** as a colorless solid: mp 92 °C; ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int) 1.56−1.86 (m); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int) 16.58 (t), 25.20 (t), 50.19 (s); MS *m/z* 216 (2, M^+), 131 (100). Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.82; H, 11.26.

13-[(1'-Methylselanyl)cyclobutyl]trispiro[3.0.3.0.3.1]tridecan-13-ol (15a). To a stirred solution of 1,1-bis(methylselanyl)cyclobutane[21] (36.3 g, 150 mmol) in anhydrous ether (150 mL) at −78 °C under nitrogen was added a 1.4 M solution of *tert*-butyllithium in pentane (107 mL, 150 mmol) such that the temperature did not exceed −60 °C (30 min). After 1 h, **10** (28.5 g, 150 mmol) was added within 30 min and stirring at −78 °C continued until GC analysis [2.5 m × 1/4 in. all glass system, 15% SE 30 on Chromosorb W AW/DMCS 60−80 mesh, 10 min 170 °C, 20 °C/min to 250 °C; relative retention times: 1.00 (**10**), 3.30 (**15a**)] indicated that **10** had been consumed (2 h). The still cold mixture was washed with saturated ammonium chloride (3 × 75 mL), the combined aqueous phases were extracted with ether (30 mL), and the combined organic phases were dried ($CaCl_2$). The solvents were evaporated (bath temperature 50 °C, 20 Torr), yielding 49.7 g (98%) of crude **15a** (purity 90%, GC) as a yellow, vile-smelling liquid. A 100 mg sample was chromatographed on silica gel (0.1−0.2 mm) in pentane/ether [9:1; column 20 × 1 cm; R_f = 0.58, 0.32, 0.22 (**15a**)], yielding 57 mg of pure **15a** as a colorless, vile-smelling liquid: ^{1}H NMR (80 MHz, $CDCl_3$, TMS int) 1.5−2.9 (m, 25), 2.14 (s, 3); ^{13}C NMR (50.3 MHz, $CDCl_3$, TMS int) 4.68 (q), 15.82 (t), 16.25 (t), 16.91 (t), 26.24 (t), 26.36 (t), 27.05 (2 t), 31.77 (t), 50.92 (s), 52.79 (s), 55.98 (s), 79.90 (s).

13-[1'-(Phenylselanyl)cyclobutyl]trispiro[3.0.3.0.3.1]tridecan-13-ol (15b). To a stirred solution of 1,1-bis(phenylselanyl)cyclobutane[21] (43.9 g, 120 mmol) in anhydrous tetrahydrofuran (120 mL) at −78 °C under nitrogen was added a 1.6 M solution of *n*-butyllithium in *n*-hexane (75 mL, 120 mmol) such that the temperature did not exceed −70 °C (1.5 h). After 1 h at −78 °C the mixture was warmed to −40 °C and treated with a solution of **10** (15.0 g, 79 mmol) in anhydrous tetrahydrofuran (80 mL) such that the temperature did not exceed −35 °C (1 h). This temperature was maintained until TLC (pentane/ether, 9:1; R_f = 0.53 (**10**), 0.40 (**15b**)) indicated that **10** had been consumed (12 h). The mixture was hydrolyzed with water (5 mL), the organic phase was washed with saturated sodium bicarbonate (2 × 80 mL), the combined aqueous phases were extracted with ether (2 × 80 mL), and the combined organic phases were dried ($MgSO_4$). The solvents were evaporated (bath temperature 50 °C, 12 Torr), and the orange, oily residue (60.5 g) was chromatographed on silica gel (0.05−0.20 mm) in pentane/ether (9:1; column 130 × 7 cm), yielding 21.7 g (68%) of **15a** as a light yellow solid: mp 72 °C; IR (KBr) (O−H) 3380 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS int) 1.63−2.10 (m, 13), 2.12−2.27 (m, 6), 2.29−2.48 (m, 4), 2.65−2.80 (m, 2), 7.30−7.40 (m, 3), 7.71−7.80 (m, 2); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int) 15.73 (t), 15.84 (t), 16.90 (t), 25.69 (s), 26.38 (t), 26.45 (t), 26.97 (t), 27.13 (t), 32.98 (t), 50.69 (s), 52.85 (s), 79.64 (s), 128.48 (d), 128.82 (d), 128.90 (s), 137.67 (d); MS *m/z* 402 (1, M^+), 137 (100). Anal. Calcd for $C_{23}H_{30}OSe$: C, 68.81; H, 7.53. Found: C, 68.95; H, 7.54.

Tetraspiro[3.0.3.0.3.0.3.1]heptadecan-17-one (11). A. From 15a with Silver Tetrafluoroborate. Protected from light, dry neutral aluminum oxide (153 g, 1.50 mol) and silver tetrafluoroborate (32.6 g, 167 mmol) were added to dry acetone (100 mL) (exothermic effect). After 5 min of stirring the solvent was evaporated und the residue dried (6 h, 100 °C, 0.01 Torr). The coated material was suspended in dry carbon tetrachloride (500 mL), and within 15 min at −20 °C under nitrogen with stirring, a solution of crude **15a** (49.6 g, 146 mmol) was added. After 21 h at −20 °C TLC (pentane/ether, 96:4; R_f = 0.67, 0.29 (**11**), 0.22, 0.11 (**15a**)) indicated that the reaction was complete. The yellow mixture was filtered through Celite and the Celite eluated with ether (6.0 L, control by TLC). The filtrate was washed with saturated sodium bicarbonate (3 × 500 mL), the aqueous phases were extracted with ether (100 mL), and the combined organic phases were dried ($CaCl_2$). The solvents were evaporated (bath temperature 30 °C, 20 Torr), and the residual yellow oil (31.6 g) was chromatograped on silica gel (0.1−0.2 mm) in pentane/ether (96:4; column 50 × 8 cm), yielding 18.6 g (52%) of **11** as a colorless solid: mp 78 °C. According to GC (2.5 m × 1/4 in. all glass system, 15% SE 30 on Chromosorb W AW/DMCS 60−80 mesh, 3 min 160 °C, 20 °C/min to 250 °C; relative retention times: 1.00 (**11**), 1.79 (**15a**)) the material was 98% pure: IR (KBr) (C═O) 1725 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int) 1.5−2.4 (m); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 15.63, 15.92, 23.36, 26.99, 50.71, 56.53, 224.25; MS *m/z* 244 (14, M^+), 134 (100). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.39; H, 9.73.

B. From 15a with *m*-Chloroperoxybenzoic Acid. To a stirred suspension of 70% *m*-chloroperoxybenzoic acid (64.0 g, 260 mmol) in dichloromethane (600 mL) was added within 30 min a solution of **15a** (16.0 g, 47 mmol) in ether (18 mL) (exothermic effect). After 5 min TLC (pentane/ether, 95:5; R_f = 0.61, 0.35 (**11**), 0.24, 0.15 (**15a**), 0.09, 0.05) indicated that the reaction was complete. The mixture was washed with 1 N NaOH (1 × 280 mL, 2 × 50 mL) and dried ($MgSO_4$). The solvent was evaporated (bath temperature 50 °C, 15 Torr) and the yellow, solid residue (17.9 g) chromatographed on silica gel (0.05−0.20 mm) in pentane/ether (97:3; column 18 × 8 cm), yielding 10.6 g (84%) of **11** (purity 92%, GC) as a light yellow solid: mp 48−62 °C.

C. From 15b with *m*-Chloroperoxybenzoic Acid. To a stirred suspension of 70% *m*-chloroperoxybenzoic acid (61.5 g, 250 mmol) in dichloromethane (800 mL) at 0 °C was added a solution of **15b** (20.0 g, 50 mmol) in dichloromethane (200 mL) such that the temperature did not exceed 5 °C. Stirring was continued at 0−5 °C until TLC [pentane/ether, 9:1; R_f = 0.59 (**11**), 0.40 (**15b**)] indicated that **15b** had been consumed (2 h). The mixture was washed with 1 N NaOH (4 × 200 mL) and dried ($MgSO_4$). The solvent was evaporated (bath temperature 50 °C, 15 Torr) and the residual yellow oil (11.4 g) chromatographed on silica gel (0.05−0.20 mm) in pentane/ether (9:1; column 130 × 7 cm), yielding 8.3 g (68%) of **11** (purity 98%, GC) as a colorless solid: mp 78 °C.

17-[1-(Methylselanyl)cyclobutyl]tetraspiro[3.0.3.0.3.0.3.1]heptadecan-17-ol (16a). To a stirred solution of **11** (18.6 g, 76.1 mmol) and 1,1-bis(methylselanyl)cyclobutane[21] (18.4 g, 76.1 mmol) in anhydrous ether (50 mL) at −30 °C under nitrogen was added over a period of 5 h a 1.4 M solution of *tert*-butyllithium in pentane (54.3 mL, 76.1 mmol) and the reaction progress monitored by TLC [pentane/ether,

97:3; R_f = 0.25 (**16a**), 0.15 (**11**)]. After 15 h at −30 °C, more 1,1-bis(methylseleno)cyclobutane (3.7 g, 15.2 mmol) and, over a period of 1 h, more of a 1.4 M solution of *tert*-butyllithium in pentane (10 mL, 14.0 mmol) were added. After an additional 18 h at −30 °C the reaction was complete. The still cold mixture was hydrolyzed with saturated ammonium chloride (30 mL) and washed with brine (30 mL). The combined aqueous phases were extracted with ether (30 mL) and the combined organic phases dried ($CaCl_2$). The solvents were evaporated (bath temperature 25 °C, 20 Torr), and the yellow, oily residue (35.0 g) was chromatographed on silica gel (0.05−0.20 mm) in pentane/ether (97:3; column 50 × 8 cm), yielding 21.1 g (70%) of pure **16a** as a colorless liquid: IR (neat) (O−H) 3620 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int) 1.50−2.70 (m, 30), 1.55 (s, 1, D_2O exchange), 2.18 (s, 3); ^{13}C NMR (50.3 MHz, $CDCl_3$, TMS int) 6.24 (q), 15.39 (t), 15.61 (t), 16.43 (t), 18.47 (t), 24.98 (t), 25.12 (t), 25.50 (t), 27.83 (t), 28.83 (t), 33.12 (t), 54.05 (s), 55.44 (s), 55.93 (s), 58.67 (s), 61.54 (s), 86.95 (s), all other signals were not visible due to coalescence phenomena; MS *m/z* 394, 392 (2, 1, M^+), 67 (100). Anal. Calcd for $C_{22}H_{34}OSe$: C, 67.16; H, 8.71. Found: C, 66.16; H, 8.49.

Pentaspiro[3.0.3.0.3.0.3.0.3.1]heneicosan-21-one (12). A. From 16a with Silver Tetrafluoroborate. Protected from light, neutral aluminum oxide (62.9 g, 617 mmol) was coated with silver tetrafluoroborate (12.0 g, 61.7 mmol) as described for **11**. The material was suspended in dry tetrachloromethane (200 mL), and then, within 1 h at −20 °C under nitrogen with stirring, a solution of **16a** (20.2 g, 51.4 mmol) in dry tetrachloromethane (100 mL) was added. Stirring was continued for 1 d at −10 °C and then at 0 °C while the reaction progress was monitored by TLC [pentane/ether, 98:2; R_f = 0.70, 0.28 (**12**), 0.22 (**16a**)]. After 5 d more silver tetrafluoroborate (3.0 g, 15.4 mmol) was added, and after an additional 2 d the reaction was complete. The now black reaction mixture was filtered through Celite, and the celite was eluated with ether (3 L, control by TLC). The filtrate was washed with saturated sodium bicarbonate (3 × 200 mL), the aqueous phases were extracted with ether (50 mL), and the combined organic phases were dried ($CaCl_2$). The solvents were evaporated (bath temperature 30 °C, 20 Torr), and the yellow, solid residue (12.9 g) was chromatographed twice on silica gel (0.05−0.20 mm) in pentane/ether (98:2; columns 50 × 8 cm, 120 × 4 cm), yielding 7.02 g (46%) of **12** as a colorless solid: mp 137−138 °C (lit.[22] mp 137−138 °C). The ^{13}C NMR data were in accord with literature data.[22]

B. From 16b with *m*-Chloroperoxybenzoic Acid. Concurrent Formation of 17-(5-Oxabicyclo[2.1.0]pent-1-yl)tetraspiro-[3.0.3.0.3.0.3.1]heptadecan-17-ol (17). To a stirred suspension of 70% *m*-chloroperoxybenzoic acid (23.0 g, 93.3 mmol) in dichloromethane (150 mL) was added within 30 min a solution of **16b** (5.91 g, 15.0 mmol) in dichloromethane (12 mL) (exothermic effect). After 5 min TLC [pentane/ether, 95:5; R_f = 0.42 (**12**), 0.17 (**17**)] indicated that the reaction was complete. The mixture was washed with 1 N NaOH (1 × 100 mL, 2 × 50 mL) and dried ($CaCl_2$). The solvents were evaporated (bath temperature 50 °C, 15 Torr), and the yellow, oily residue (5.1 g) was chromatographed on silica gel (0.05−0.20 mm) in pentane/ether (95:5; column 30 × 4 cm), yielding 1.59 g (36%) of **12** as a colorless solid, mp 127−129 °C, and 1.53 g (32%) of **17** as a light yellow, slowly crystallizing oil. Analytically pure **17** was obtained by 2-fold crystallization from acetone as a colorless solid: mp 71−76 °C; IR (KBr) (O−H) 3510 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int) 1.4−2.7 (m, 28), 2.3 (s, H, D_2O exchange), 3.9−4.0 (m, 1); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 15.85, 16.38, 16.56, 17.29, 24.28, 24.94, 25.17, 25.35, 25.56 (coincidence of two lines), 26.35, 26.66, 28.69, 31.44, 54.72, 54.75, 56.41, 57.23, 58.06, 69.45, 80.18; MS *m/z* 314 (0.02, M^+), 91 (100). Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.37; H, 9.64.

17-Methylentetraspiro[3.0.3.0.3.0.3.1]heptadecane (18). To a stirred suspension of potassium *tert*-butoxide (5.88 g, 52.5 mmol) in anhydrous benzene (120 mL) under nitrogen was added methyltriphenylphosphonium bromide (18.8 g, 52.5 mmol) and the mixture heated to reflux. After 2 h, **11** (2.57 g, 10.5 mmol) was added and most of the solvent distilled off under nitrogen until the bath temperature reached 130 °C. This temperature was maintained until GC analysis [1.2 m × 1/4 in. all glass system, 15% OV 210 on Chromosorb W AW/DMCS 60−80 mesh, 190 °C; relative retention times: 1.00 (**18**), 2.79 (**11**)] indicated that the reaction was complete (20 h). The mixture was diluted with pentane (55 mL) and hydrolyzed with water (3.5 mL). The organic phase was decanted and the residue extracted with pentane (3 × 30 mL). The combined organic phases were washed with water (3 × 25 mL) and dried ($MgSO_4$). The solvent was evaporated (bath temperature 20 °C, 15 Torr) and the residue (4.56 g) chromatographed on silica gel (0.1−0.2 mm) in pentane (column 15 × 5 cm; R_f = 0.61), yielding 2.14 g (84%) of pure **18** as a colorless liquid: IR (neat) (C═C) 1640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int) 0.80−2.20 (m, 24), 5.33 (s, 2); ^{13}C NMR (126 MHz, $CDCl_3$, $CDCl_3$ int) 15.46 (t), 15.92 (t), 23.55 (t), 31.56 (t), 53.54 (s), 53.60 (s), 101.76 (t), 171.60 (s); MS *m/z* 242 (1, M^+), 171 (100). Anal. Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 89.10; H, 10.71.

Pentaspiro[2.0.3.0.3.0.3.0.3.0]nonadecane-1-carboxylic Acid Methyl Ester (19). To a stirred solution of **11** (738 mg, 3.04 mmol) in cyclohexane (1.5 mL) under nitrogen was added electrolyte copper (190 mg, 2.99 mmol) and the mixture heated to 110 °C. Dropwise addition of diazoacetic acid methyl ester (1.22 g, 12.2 mmol) caused a concomitant gas evolution which subsided until the addition was complete. The mixture was filtered, the filtrate concentrated (bath temperature 20 °C, 15 Torr), and the yellow, oily residue (640 mg) chromatographed on silica gel (0.05−0.20 mm) in pentane/ether [95:5; column 30 × 3 cm; R_f = 0.66 (**11**), 0.26 (**19**)], yielding 225 mg (31%) of unchanged **11** and 211 mg (22%) of pure **19** as a colorless solid: mp 65 °C; IR (KBr) (C═O) 1730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, TMS int) 1.18 (dd, 1, J = 9, 5 Hz), 1.37−1.86 (m, 15), 1.97 (dd, 1, J = 9, 8 Hz), 2.01−2.32 (m, 10), 3.72 (s, 3); ^{13}C NMR (50.3 MHz, $CDCl_3$, TMS int) 15.92 (t), 15.94 (t), 16.05 (t), 16.53 (t), 16.84 (t), 23.61 (d), 24.53 (t), 24.96 (t), 25.07 (t), 25.16 (t), 27.48 (t), 28.57 (t), 29.15 (t), 29.42 (t), 48.27 (s), 51.62 (s), 51.78 (q), 53.87 (s), 54.40 (s), 55.39 (s), 173.68 (s); MS *m/z* 200 (100), 157 (70). Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.61. Found: C, 80.14; H, 9.57.

Pentaspiro[2.0.3.0.3.0.3.0.3.0]nonadecane-1-methanol (20). To a stirred suspension of lithium aluminum hydride (55 mg, 1.25 mmol) in anhydrous ether (1 mL) at room temperature under nitrogen was added within 5 min a solution of **19** (266 mg, 0.85 mmol) in anhydrous ether (1 mL). After 10 min TLC [dichloromethane; R_f = 0.67 (**19**), 0.47, 0.29 (**20**)] indicated that the reaction was complete. The mixture was treated with water (50 μL), a 15% aqueous solution of sodium hydroxide (50 μL), and water (160 μL), the organic phase was decanted, and the residue was extracted with ether (10 × 1.5 mL, control by TLC). The combined organic phases were concentrated (bath temperature 25 °C, 15 Torr), and the colorless, solid residue was chromatographed on silica gel (0.05−0.20 mm) in dichloromethane (column 17 × 1.3 cm), yielding 284 mg (99%) of pure **20** as a colorless solid: mp 49 °C; IR (KBr) (O−H) 3340 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int) 0.60−0.93 (m, 2), 1.50 (s, 1, D_2O exchange), 1.20−2.30 (m, 25), 3.75−4.10 (m, 2); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 14.01, 15.40, 15.64, 16.08, 16.47, 24.15, 24.32, 24.95, 25.29, 25.51, 27.95, 28.24, 29.22, 29.65, 41.73, 51.95, 53.12, 54.55, 55.58, 63.22; MS *m/z* 286 (2, M^+), 200 (100). Anal. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 83.65; H, 10.47.

Pentaspiro[2.0.3.0.3.0.3.0.3.0]nonadecane-1-carbaldehyde (21). To a stirred solution of oxalyl chloride (140 mg, 1.10 mmol) in anhydrous dichloromethane (2.5 mL) at −60 °C under nitrogen was added a solution of dimethyl sulfoxide (44 mg, 0.56 mmol) in anhydrous dichloromethane (0.5 mL). After 2 and 15 min, respectively, a solution of **20** (284 mg, 0.99 mmol) in anhydrous dichloromethane (1.0 mL) and triethylamine (507 mg, 5.01 mmol) were added. After a further 10 min at −60 °C the colorless suspension was warmed to room temperature and hydrolyzed with water (5 mL). The layers were separated, the aqueous phase was extracted with dichloromethane (5 mL), and the combined organic phases were washed with brine (10 mL) and dried (molecular sieves 4 Å). Evaporation of the solvent (bath temperature 20 °C, 15−0.5 Torr) yielded 284 mg (100%) of crude **21** as a yellow liquid. This material was used as such as an attempt of a chromatographic purification on silica gel in dichloromethane led to a mixture of rearranged aldehydes: IR (neat) (C═O) 1690 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$, $CHCl_3$ int) 0.50−2.50 (m, 27), 9.45 (d, 1, J = 7 Hz); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 14.87 (t), 15.54 (t), 15.76 (t), 16.29 (t), 18.84 (t), 24.37 (t), 24.63 (t), 24.86 (t), 24.97 (t), 27.19

(t), 28.66 (t), 28.71 (t), 32.07 (t), 35.03 (d), 51.33 (s), 51.75 (s), 53.67 (s), 54.23 (s), 54.99 (s), 200.68 (d); MS *m/z* 284 (33, M^+), 227 (100). HRMS *m/z* (M^+) calcd 284.2140, obsd 284.2140.

Pentaspiro[3.0.3.0.3.0.3.0.3.0]eicos-1-ene (23) via *N*-Pentaspiro-[2.0.3.0.3.0.3.0.3.0]nonadec-1-ylidene-*N*'-(*p*-tosyl)hydrazine (22). Concurrent Formation of 17-Methylenetetraspiro[3.0.3.0.3.0.3.1]-heptadecane (18). To a stirred solution of crude **21** (170 mg, 0.60 mmol) in anhydrous dichloromethane (1.0 mL) at 0 °C were added anhydrous triethylamine (61 mg, 0.60 mmol) and tosyl hydrazide (112 mg, 0.60 mmol). The reaction was monitored by TLC [ether; R_f = 0.66 (**21**), 0.58 (**22**), 0.41, 0.33 (tosyl hydrazide)], and after 21 and 30 h at 0 °C, more tosyl hydrazide (45 mg, 0.24 mmol) and triethylamine (31 mg, 0.30 mmol) were added. After 42 h at 0 °C, all **21** had been consumed. The mixture was warmed to room temperature, dried (molecular sieves 4 Å), and concentrated (bath temperature 20 °C, 15−0.5 Torr), yielding 370 mg of crude **22** as a viscous yellow liquid. The crude **22** was dissolved in anhydrous diethylene glycol dimethyl ether (2.0 mL) and the solution treated with sodium methoxide (162 mg, 3.00 mmol) under nitrogen at 130 °C. A gas evolution was observed, and after 5 min TLC [ether; 0.69 (**23**, **18**), 0.58 (**22**), 0.36] indicated that the reaction was complete. The mixture was filtered through silica gel (0.05−0.20 mm) in pentane and concentrated (bath temperature 20 °C, 15 Torr) and the yellow, oily residue (130 mg) chromatographed on silica gel (0.05−0.20 mm) in pentane [column 30 × 1.5 cm; R_f = 0.62 (**23**), 0.57 (**18**)], yielding 57 mg of a 3:1 mixture of **23** and **18** as a colorless solid (mp 105 °C). This material was used for the preparation of **7**. Nearly pure **23** was obtained by repeated chromatography on silica gel in pentane: ^{1}H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int) 0.65−2.45 (m, 24; 0.65−1.40 pentane), 2.30 (d, 2, J = 0.95 Hz), 6.07 (d, 1, J = 2.85 Hz), 6.28 (td, 1, J = 2.85, 0.95 Hz).

Pentaspiro[3.0.3.0.3.0.3.0.3.0]eicosane ([5.4]Rotane) (7). A stirred solution of a 3:1 mixture of **23** and **18** (56 mg) in pentane (1.5 mL) at 20 °C was hydrogenated at 1.1 atm of H_2 over 10% Pd/C (50 mg) until TLC [pentane; R_f = 0.64 (**7**), 0.62 (**23**), 0.57 (**18**)] indicated that **23** had been consumed (1 h). Chromatography on silica gel (0.05−0.20 mm) in pentane (column 7.0 × 0.6 cm) yielded 54 mg of a viscous, colorless liquid. Preparative GC [1.2 m × 1/4 in. all glass system, 15% OV 210 on Chromosorb W AW/DMCS 60−80 mesh, 180 °C; relative retention times: 0.27, 0.38, 0.63, 0.76, 1.00 (**7**)] gave 11.4 mg (27%) of **7** as a colorless solid, mp 70−110 °C. Recrystallization from methanol gave colorless crystals: ^{1}H NMR (200 MHz, CD_2Cl_2, $CHDCl_2$ int) 1.66−1.88 (m, 10, 1.96−2.10 (m, 20); ^{13}C NMR (50.3 MHz, CD_2Cl_2, CD_2Cl_2 int) 16.78, 27.40, 55.30; MS *m/z* 270 (14, M^+), 147 (100); HRMS *m/z* (M^+) calcd 270.2348, obsd 270.2348.

21-Methylenepentaspiro[3.0.3.0.3.0.3.0.3.1]heneicosane (24). To a stirred suspension of potassium *tert*-butoxide (3.77 g, 33.6 mmol) in anhydrous benzene (70 mL) at room temperature under nitrogen was added methyltriphenylphosphonium bromide (12.00 g, 33.6 mmol) and the mixture heated to reflux. After 2 h, a solution of **12** (980 mg, 3.29 mmol) in anhydrous benzene (6 mL) was added and most of the solvent distilled off under nitrogen until the bath temperature reached 130 °C. This temperature was maintained until TLC [pentane/ether, 99:1; R_f = 0.64 (**24**), 0.33, 0.24 (**12**)] indicated that the reaction was complete (63 h). The reaction mixture was diluted with pentane (70 mL) and hydrolyzed with water (7 mL) and the organic phase decanted. The residue was extracted with pentane (3 × 20 mL), and the combined organic phases were washed with water (3 × 20 mL), dried ($MgSO_4$), and concentrated (bath temperature 50 °C, 50 Torr). The residue (5.9 g) was chromatographed on silica gel (0.05−0.20 mm) in pentane (column 35 × 3 cm), yielding 540 mg (55%) of **24** as a colorless solid, mp 165−181 °C (lit.[7c] mp 192−195 °C).

[21-*methylene*-^{13}C]Pentaspiro[3.0.3.0.3.0.3.0.3.1]heneicosane ([*methylene*-^{13}C]-24). Methylenation of **12** (0.50 g, 1.7 mmol) with ([^{13}C]-methyl)triphenylphosphonium iodide[35] (9.50 g, 23.5 mmol, 99% ^{13}C) and potassium *tert*-butoxide (2.63 g, 23.5 mmol), analogous to the preparation of **24**, gave 216 mg (43%) of [*methylene*-^{13}C]**24**: ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int) 1.08−2.58 (m, 30), 5.20 (d, 2, J = 154 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int) 108.53.

Hexaspiro[2.0.3.0.3.0.3.0.3.0]tricosane-1$_{eq}$-carboxylic Acid Methyl Ester (25) and Hexaspiro[2.0.3.0.3.0.3.0.3.0]tricosane-1$_{ax}$-carboxylic Acid Methyl Ester (25'). To a stirred solution of **24** (540 mg, 1.82 mmol) in cyclohexane (0.9 mL) under nitrogen was added electrolyte copper (200 mg, 3.15 mmol) and the mixture heated to 110 °C. Dropwise addition of diazoacetic acid methyl ester (1.85 g, 18.5 mmol) caused a concomitant gas evolution which subsided until the addition was complete (2.5 h). TLC [pentane/ether, 98:2; R_f = 0.64 (**24**), 0.16 (**25'**), 0.11 (**25**)] indicated the formation of two products. The mixture was diluted with ether (12 mL), filtered, and concentrated (bath temperature 20 °C, 15 Torr) and the residue chromatographed on silica gel (0.1−0.2 mm) in pentane/ether (98:2; column 22 × 2 cm) yielding 320 mg (59%) of unchanged **24**, 132 mg (20%) of a mixture of **25** and **25'**, and 109 mg (16%) of pure **25**. Chromatography of the mixture of **25** and **25'** yielded 46 mg (7%) of **25**, mp 130−134 °C, and 36 mg (5%) of **25'**, mp 147−151 °C, as colorless solids. Data for **25**: IR (KBr) (C═O) 1730 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int) 0.8−2.9 (m, 33), 3.78 (s, 3); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 11.90, 15.65, 16.25, 16.43, 16.51, 16.75, 18.80, 25.27, 25.34, 25.38, 25.88, 26.34, 26.56, 27.89, 28.61 (coincidence of two lines), 28.77, 34.06, 47.95, 49.16, 49.78, 50.72, 51.16, 51.90, 173.39; MS *m/z* 240 (66), 91 (100). Data for **25'**: IR (KBr) (C═O) 1735 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int) 1.0−3.0 (m, 33), 3.50 (s, 3); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 9.16, 16.18, 16.30, 16.49, 16.77, 16.80, 25.11, 25.33 (coincidence of two lines), 26.00, 26.15, 26.34, 27.20 (coincidence of two lines), 28.75 (coincidence of two lines), 31.27, 36.68, 49.41, 50.02, 50.23, 50.39, 50.59, 51.55, 174.14; MS *m/z* 240 (59), 197 (100). Anal. Calcd for $C_{25}H_{36}O_2$: C, 81.47; H, 9.85. Found: C, 81.57; H, 9.95.

[2-^{13}C]-Hexaspiro[2.0.3.0.3.0.3.0.3.0]tricosane-1$_{eq}$-carboxylic Acid Methyl Ester ([2-^{13}C]25) and [2-^{13}C]Hexaspiro-[2.0.3.0.3.0.3.0.3.0]tricosane-1$_{ax}$-carboxylic Acid Methyl Ester ([2-^{13}C]25'). Under the conditions described for the preparation of **25** and **25'**, [*methylene*-^{13}C]**24** (316 mg, 1.10 mmol) yielded 162 mg (51%) of unchanged [*methylene*-^{13}C]**24**, 81 mg (30%) of [2-^{13}C]**25**, and 31 mg (12%) of [2-^{13}C]**25'**. Data for [2-^{13}C]**25**: ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int) 0.48−2.74 (m, 33), 3.80 (s, 3); ^{13}C NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int) 11.95. Data for [2-^{13}C]**25'**: ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int) 0.74−2.78 (m, 33), 3.53 (s, 3); ^{13}C NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int) 9.17.

Hexaspiro[2.0.3.0.3.0.3.0.3.0]tricosane-1$_{eq}$-methanol (26). To a stirred suspension of lithium aluminum hydride (31 mg, 0.82 mmol) in anhydrous ether (1.0 mL) at room temperature under nitrogen was added within 2 min a solution of **25** (109 mg, 0.30 mmol) in anhydrous ether (1.5 mL). Stirring was continued until TLC [dichloromethane; R_f = 0.62 (**25**), 0.31, 0.22 (**26**)] indicated that the reaction was complete (50 min). The mixture was treated with water (31 μL), a 10% aqueous solution of sodium hydroxide (46 μL), and water (72 μL), the organic phase was separated, and the residue was extracted with ether (10 × 1 mL, control by TLC). The combined organic phases were concentrated (bath temperature 25 °C, 15 Torr), and the colorless, solid residue (95 mg) was chromatographed on silica gel (0.05−0.20 mm) in dichloromethane (column 16 × 1.3 cm), yielding 85 mg (83%) of pure **26** as a colorless solid: mp 136−185 °C; IR (KBr) (O−H) 3400 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int) 0.6−2.9 (m, 34), 1.4 (dd, 1, J = 5 Hz, D_2O exchange), 4.2−4.4 (m, 2); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 11.15, 15.29, 16.54 (coincidence of three lines), 16.83, 18.53, 25.22, 25.47, 25.62, 25.67, 26.50, 28.00, 28.27, 28.76, 28.91, 29.00, 29.62, 47.47, 49.17, 49.77, 50.61, 51.28, 61.37; MS *m/z* 91 (100).

[2-^{13}C]Hexaspiro[2.0.3.0.3.0.3.0.3.0]tricosane-1$_{eq}$-methanol ([2-^{13}C]26). Under the conditions described for the preparation of **26**, reduction of [2-^{13}C]-**25** (79 mg, 0.21 mmol) with lithium aluminum hydride (28 mg, 0.74 mmol) yielded 62 mg (86%) of [2-^{13}C]**26**: ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int) 0.71 (ddd, 1, J = 154, 9, 5.5 Hz), 0.72 (ddd, 1, J = 159, 12, 5.5 Hz), 1.80−2.36 (m, 32), 4.28 (ddd, 1, J = 11, 8, 2.5 Hz), 4.40 (ddd, 1, J = 11, 6, 5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, $CDCl_3$ int) 11.17.

Hexaspiro[2.0.3.0.3.0.3.0.3.0]tricosane-1$_{eq}$-carbaldehyde (27). To a stirred solution of oxalyl chloride (40 mg, 0.31 mmol) in anhydrous

(35) ([^{13}C]Methyl)triphenylphosphonium iodide (99 atom % ^{13}C, mp 176 °C) was obtained by reacting triphenylphosphine (70 mmol) in dry benzene (60 mL) with [^{13}C]methyl iodide (70 mmol, 99 atom % ^{13}C) for 72 h at room temperature (yield 98%).

Table 2. Crystal Data and Structure Refinement Details for **6**−**8**

	6	**7**	**8**
formula	$C_{16}H_{24}$	$C_{20}H_{30}$	$C_{24}H_{36}$
molecular weight	216.35	270.44	324.53
crystal system	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	*C*2/*c*	$P\bar{1}$
color of crystal	colorless	colorless	colorless
crystal size (mm)	0.60 × 0.50 × 0.45	0.60 × 0.50 × 0.35	0.60 × 0.50 × 0.20
a (Å)	13.619(3)	22.859(5)	7.666(2)
b (Å)	8.230(2)	9.513(2)	7.983(1)
c (Å)	12.452(3)	14.725(3)	8.208(2)
α (deg)	90	90	69.08(1)
β (deg)	115.24(3)	102.96(3)	74.08(1)
γ (deg)	90	90	76.60(1)
V (Å^3)	1262.4(5)	3120.5(11)	446.17(17)
Z	4	8	1
D_{calcd} (g/cm^3)	1.138	1.151	1.208
μ (mm^{-1})	0.063	0.064	0.067
F(000)	480	1200	180
T (K)	133(2)	133(2)	133(2)
2*θ* range (deg)	6.0−66.4	4.7−55.9	5.4−59.6
no. of rflns colld	13610	19601	5947
no. of indep rflns	2401	3722	2320
R(int)	0.0201	0.0284	0.0231
no. of data	2401	3722	2320
no. of params	122	303	183
no. of restraints	27	135	54
goodness of fit	1.074	1.055	1.047
R_1 [$I > 2(I)$]	0.0393	0.0496	0.0409
wR_2 (all data)	0.1064	0.1228	0.1149
extinction coefficient		0.0016(3)	0.073(15)
g_1	0.0581	0.0454	0.0617
g_2	0.4277	3.1424	0.1330
largest diff peak	0.370	0.339	0.321
largest diff hole (e Å^{-3})	−0.185	−0.192	−0.215

dichloromethane (650 *μ*L) at −60 °C under nitrogen was added a solution of dimethyl sulfoxide (48 mg, 0.62 mmol) in anhydrous dichloromethane (130 *μ*L). After 2 and 20 min, respectively, a solution of **26** (79 mg, 0.23 mmol) in anhydrous dichloromethane (2 mL) and triethylamine (131 mg, 1.29 mmol) were added. After a further 15 min at −60 °C the colorless suspension was warmed to room temperature and hydrolyzed with water (1.5 mL). The layers were separated, the aqueous phase was extracted with dichloromethane (2 × 1.5 mL), and the combined organic phases were washed with brine (3 mL) and dried (molecular sieves 4 Å). Evaporation of the solvent (bath temperature 20 °C, 15 Torr) yielded 55 mg (71%) of **27** as a colorless solid: IR (KBr) (C═O) 1730, 1695 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int) 1.1−3.0 (m, 33), 10.0 (d, 1, J = 5 Hz); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 14.52, 15.41, 16.10, 16.43 (coincidence of two lines), 16.57, 25.09, 25.31 (coincidence of two lines), 26.01, 27.00, 27.87, 28.66, 29.01 (coincidence of two lines), 29.16, 29.52, 40.62, 48.13, 48.93, 50.29, 50.79, 51.20, 201.59; MS *m/z* 338 (1, M$^+$), 86 (100). HRMS *m/z* (M$^+$) calcd 338.2610, obsd 338.2610.

[2-^{13}C]Hexaspiro[2.0.3.0.3.0.3.0.3.0.3.0]tricosane-1$_{eq}$-carbaldehyde ([2-^{13}C]27). Under the conditions described for the preparation of **27**, oxidation of [2-^{13}C]**26** (58 mg, 0.17 mmol) with oxalyl chloride (28 mg, 0.22 mmol), dimethyl sulfoxide (34 mg, 0.44 mmol), and triethylamine (91 mg, 0.90 mmol) yielded 53 mg (92%) of [2-^{13}C]**27**: ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int) 1.04−2.70 (m, 33), 10.04 (dd, 1, J = 5, 0.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, $CDCl_3$ int) 15.54.

Hexaspiro[3.0.3.0.3.0.3.0.3.0.3.0]tetracos-1-ene (29) via *N*-Hexaspiro[2.0.3.0.3.0.3.0.3.0.3.0]tricosan-1-ylidene-*N*'-(*p*-tosyl)hydrazine (28). To a solution of crude **27** (55 mg, 0.16 mmol) in anhydrous dichloromethane (0.5 mL) were added anhydrous triethylamine (12 mg, 0.12 mmol) and tosyl hydrazide (60 mg, 0.32 mmol), and the mixture was stirred at room temperature until ^{1}H NMR analysis revealed that the resonance of the aldehyde proton of **27** had disappeared (44 h). The mixture was concentrated (bath temperature 20 °C, 15 Torr), the residue (114 mg) containing the crude **28** dissolved in anhydrous diethylene glycol dimethyl ether (0.7 mL), and the solution treated with sodium methoxide (57 mg, 1.06 mmol) under nitrogen at 130 °C. A gas evolution was observed, and after 5 min TLC [ether; 0.76 (**29**), 0.64 (**28**)] indicated that **28** had been consumed. The mixture was cooled and chromatographed on silica gel (0.05−0.20 mm) in pentane [column 22 × 1.8 cm; R_f = 0.58 (**29**), 0.53, 0.47], yielding 22 mg of a colorless, partially crystallized oil. Crystallization from dichloromethane yielded 10 mg (19%) of **29** as a colorless solid: mp 175−188 °C; ^{1}H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int) 1.35−2.90 (m, 32), 6.20 (dt, 1, J = 3, 1 Hz), 6.57 (d, 1, J = 3 Hz); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 16.10, 16.46, 16.57, 24.91, 25.16, 26.96, 27.15, 27.88, 28.03, 35.22, 47.99, 49.25, 49.69, 57.45, 135.39, 140.91; MS *m/z* 322 (2, M$^+$), 75 (100); HRMS *m/z* (M$^+$) calcd 322.2661, obsd 322.2661.

[3-^{13}C]Hexaspiro[3.0.3.0.3.0.3.0.3.0.3.0]tetracos-1$_{eq}$-ene ([3-^{13}C]-29) via [2-^{13}C]-*N*-Hexaspiro[2.0.3.0.3.0.3.0.3.0.3.0]tricosan-1$_{eq}$-ylidene-*N*'-(*p*-tosyl)hydrazine ([2-^{13}C]28). To a solution of crude [2-^{13}C]**27** (51 mg, 0.15 mmol) in anhydrous dichloromethane (0.4 mL) was added anhydrous tosyl hydrazide (58 mg, 0.32 mmol) and the mixture stirred at room temperature until TLC [ether; R_f = 0.76, 0.70 ([2-^{13}C]**27**), 0.64 ([2-^{13}C]**28**), 0.55, 0.47, 0.32] indicated that [2-^{13}C]-**27** had been consumed (40 h). The mixture was concentrated (bath temperature 25 °C, 15−0.01 Torr), yielding 87 mg of crude [2-^{13}C]**28** which was dissolved in diethylene glycol dimethyl ether (0.5 mL) and converted with sodium methoxide (80 mg, 1.10 mmol) to [3-^{13}C]**29** as described for **29**. Low-temperature crystallization of the crude material (25 mg) from dichloromethane yielded 5 mg (10%) of pure [3-^{13}C]**29** as a colorless solid: ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int) 1.48−2.66 (m, 30), 2.11 (dd, 2, J = 137, 1 Hz), 6.25 (ddt, 1, J = 5, 3, 1 Hz), 6.61 (dd, 1 J = 12.5, 3 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, $CDCl_3$ int) 35.21.

Hexaspiro[3.0.3.0.3.0.3.0.3.0.3.0]tetracosane ([6.4]Rotane) (8). To a stirred solution of **29** (9 mg, 0.025 mmol; purity 90%, GC) in anhydrous pentane (2 mL) was added 10% Pd/C (50 mg) and the mixture hydrogenated at 1.1 atm of H_2 until GC analysis [1.8 m × 1/4 in. all glass system, 2% SE 30 on Chromosorb W AW/DMCS 60−80 mesh, 205 °C; relative retention times: 1.0, 1.7 (**29**), 2.2 (**8**)] indicated that **29** had been consumed (60 min). Filtration through silica gel

(0.05−0.20 mm) in pentane and evaporation of the solvent yielded 9 mg (99%) of crude **8** (purity 90%, GC) as a colorless solid. Analytically pure **8** was obtained by recrystallization from trichloromethane as a colorless solid: mp 274 °C (closed capillary); ^{1}H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int) 1.5−2.2 (m, 24), 2.9−3.3 (m, 12); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int) 16.76, 25.65, 28.53, 49.79; MS *m/z* 91 (100).

[1_{eq},2-D_2]Hexaspiro[3.0.3.0.3.0.3.0.3.0]tetracosane ([1_{eq},2-D_2]-[6.4]Rotane) ([1,2-D_2]8). Under the conditions described for the preparation of **8**, deuteration of **29** (6 mg, 0.019 mmol, purity 80%, GC) yielded 4 mg (83%) of pure [1,2-D_2]**8**. ^{2}H NMR (30.7 MHz, $CDCl_3$, $CDCl_3$ int) 1.70 (br s, 1), 2.52 (br s, 1).

[1-$^{13}C_{ax}$]Hexaspiro[3.0.3.0.3.0.3.0.3.0]tetracosane([1-$^{13}C_{ax}$][6.4]-Rotane) ([1-^{13}C]8'). Under the conditions described for the preparation of **8**, hydrogenation of [3-^{13}C]**29** (5 mg, 15 μmol) yielded 4 mg (78%) of pure [1-^{13}C]**8'**: ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int) 1.77−2.09 (m, 24), 2.63−2.69 (m, 12); ^{13}C NMR (126 MHz, $CDCl_3$, $CDCl_3$ int) 16.76 (t), 25.64 (t), 28.52 (t), 49.76 (s); ^{13}C NMR (126 MHz, 1,3-bis-([D_3]methoxy)benzene, 1,3-bis([D_3]methoxy)benzene int) 17.08, 26.01 (C-1), 28.82, 50.18.

1,3-Bis([D_3]methoxy)benzene (30). To a solution of sodium ethoxide in ethanol, prepared from sodium (4.00 g, 170 mmol) and ethanol (190 mL), were added under nitrogen with stirring a solution of 1,3-dihydroxybenzene (9.4 g, 85 mmol) in ethanol (40 mL) and [D_3]-methyl iodide (25 g, 170 mmol). After 5 h of reflux most of the ethanol (200 mL) was distilled off and the residue poured into a 50% aqueous solution of sodium hydroxide (70 mL). The mixture was extracted with ether (3 × 200 mL), and the combined extracts were washed with water (4 × 50 mL) and dried ($CaCl_2$). The solvent was evaporated and the residue fractionated, yielding 3.4 g of a colorless liquid (bp 105−116 °C, 16 Torr) which was chromatographed on silica gel (0.1−0.2 mm) in pentane/ether [9:1; column 30 × 3 cm; R_f = 0.48, 0.39 (**30**), 0.24, 0.17, 0.12, 0.05], yielding 3.0 g of crude **30**. Preparative GC of 2.4 g of crude **30** [2 m × 1/4 in. all glass system, 15% FFAP on Chromosorb W AW/DMCS 60−80 mesh, 140 °C; relative retention times: 1.00 (**30**), 1.14, 1.20] gave 0.9 g (7%) of pure **30**: ^{1}H NMR (60 MHz, $CDCl_3$, TMS int) 6.3−7.7 (m, 4); ^{13}C NMR (126 MHz, $CDCl_3$, $CDCl_3$ int) 54.05 (hept), 100.29, 105.92, 129.68, 160.76.

X-ray Structure Determinations for 6−8. Data were collected at 140 °C on a Stoe-Siemens-Huber diffractometer with monochromated Mo K radiation (=0.710 73 Å) by using a SMART-CCD area detector. For the integration of intensities the program SAINT was used. A semiempirical absorption correction was employed for structures **6**−**8**. The structures were solved by direct methods using SHELXS-97.[36] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined freely with isotropic displacement parameters. CH distances and HH 1,3-distances were restrained to be equal. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-97, including the isotropic extinction correction.[37] The *R* values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$. ORTEP plots (50% probability displacement ellipsoids, hydrogen atoms omitted) are shown in Figure 1. Crystal data and structure refinement details are listed in Table 2.

Rate Law of the Equilibration of [1-^{13}C]8'. The rate law for a reversible, energetically degenerate first-order reaction like the equilibration of [1-^{13}C]**8'** is given by $-\ln(A - A_e)/(A_o - A_e) = 2kt$ (1), where A_o, A, and A_e refer to the initial, actual, and equilibrium concentrations, respectively.[38] In the case of [1-^{13}C]**8'** the initial and equilibrium concentrations are A_o = 100% = 1 (2) and $A_e = A_o/2$ = 1/2 (3), respectively. Insertion of (2) and (3) into (1) yields $-\ln(2A - 1) = 2kt$ (4). In many cases, the integrals of appropriate resonance lines are a direct measure for A and A_o. However, because of the presence of magnetically equivalent labeled und unlabeled positions, the situation in [1-^{13}C]**8'** is different. If the equilibration of [1-^{13}C]**8'** has reached a degree x ($0 \le x \le 1$), the integrals I' and I for the resonance lines of the axial and equatorial carbon atoms, respectively, are composed as follows: $I' = (m + 5p)(1 - x) + 6px$ (5) and $I = (m + 5p)x + 6p(1 - x)$ (6), with $m = 0.99$ and $p = 0.01$, where m and p denominate the degree of ^{13}C in the labeled and unlabeled positions, respectively. The sum of the integrals is $I + I' = 11p + m$ (7), and by dividing (6) by (7), it follows that $x = [(11p + m)I/(I + I') - 6p]/(m - p)$ (8). Taking into account that $A = A_o - x = 1 - x$, it follows from (4) that $-\ln[2(1 - x) - 1] = 2kt$ (9). Insertion of (8) into (9) yields $-\ln(K_1 - K_2[I/(I + I')]) = 2kt$ (10) with $K_1 = 1 + 12p/(m - p)$ and $K_2 = 2(11p + m)/(m - p)$. This is the rate law of the equilibration of [1-^{13}C]**8'**.

Kinetic Measurements. A precision 5 mm o.d. NMR tube (No. 507 PP, Wilmad Glass Co.) was filled with a solution of 2.0 mg of [1-^{13}C]**8'** in 400 L of 1,3-bis([D_3]methoxy)benzene and heated in a thermostated silicone bath (Haake Thermosistor TP 24) to 214 ± 3 °C. At intervals of 22 (three measurements), 32 (two measurements), and 62 min (one measurement) the probe was chilled to 50 °C and a ^{13}C NMR spectrum taken (125.9 MHz, 256 transients, acquisition time 1.193 s, pulse width 41°). After additional 17 h at 214 ± 3 °C the equilibration was complete while a final spectrum indicated an intensity ratio $I/I' = 1.02$. Supposing an incomplete relaxation of one or both nuclei, the acquisition time was set to 60 s and indeed, the intensity ratio changed to $I/I' = 1.00$. Therefore, all intensities I were corrected by a factor of 0.98 until they were used in the kinetic analysis according to (10). The least-squares adjustment of the rate data was done with the program ACTPAR.[39]

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Supporting Information Available: Tables of X-ray crystal data, non-hydrogen atomic coordinates and their anisotropic displacement parameters, bond lengths, bond angles, torsion angles, and hydrogen coordinates and their isotropic displacement parameters for **6**−**8** and **25'** (32 pages). See any current masthead page for ordering and Internet access instructions.

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