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Cyclopropyl building blocks in organic synthesis. Part 81: Striving for unusually strained oxiranes: epoxidation of spirocyclopropanated methylenecyclopropanes☆

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Dedicated to Professor Waldemar Adam on the occasion of his 65th birthday

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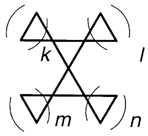
Abstract—1-Oxa[3]triangulane **13**, the epoxide of methylenespiropentane, is thermally stable up to 300°C, but immediately rearranges to spiro[2.3]hexan-4-one (**7**) in the presence of lithium iodide at ambient temperature. The permethylated bicyclopropylidene **10** is simply less reactive than the parent bicyclopropylidene (**6a**) towards dimethyldioxirane, but yields the isolable epoxide **11** (94%) with *m*CPBA. In contrast, the partially or fully spirocyclopropanated bicyclopropylidenes **18**, **20**, and **22**, upon treatment with *m*CPBA or dimethyldioxirane, did not furnish the corresponding epoxides, but underwent oxidation with rearrangement to the corresponding cyclobutanones **19**, **21** and **23** in yields of 59, 100 and 97%, respectively.

1. Introduction

The chemical properties of systems containing three-membered rings may be profoundly different from those of larger rings or acyclic analogs.[2,3] The pronounced tendency to undergo ring-opening reactions is a consequence of the ring strain and the peculiar type of bonding in cyclopropane and its heterocyclic analogues. The chemical reactivity of a three-membered ring may even be enhanced when it is either conjugated with an appropriate electronically active substituent[4–6] or its overall strain[7] is increased by incorporation into an oligocyclic molecule in such a way that it shares one atom (spirofusion) or two (annelation) with another small ring, especially another three-membered ring. Among such systems, the highly strained, so-called [*n*]triangulanes **1**, hydrocarbons which consist of spiroannelated cyclopropane rings only, and their functionally substituted derivatives, have been and still are of special interest.[8a] It turns out that all of these hydrocarbons are relatively stable towards heating and a variety of chemical reagents in spite of their high overall strain energies. The all-carbon [*n*]triangulanes therefore have become one of the most convincing examples for the notion that total strain energy of a molecule and kinetic instability do not correlate at all.[2,3] However, this principle does not necessarily apply to the corresponding heterotriangulanes **2**. Oxaspiropentane (**3a**) and azaspiropentane (**3b**) are both much more reactive[8] than the hydrocarbon spiropentane. Since little is known about the heterocyclic analogues **2** of the higher [*n*]triangulanes **1**, we studied the epoxidation of some spirocyclopropanated methylenecyclopropanes **4** and bicyclopropylidenes **5** and present our results here.



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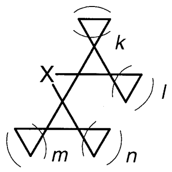
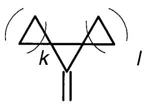


2 X = O, S, NR

3a X = O
3b X = NR



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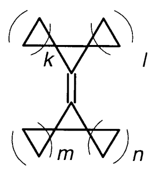

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2. Results and discussion

The simplest oxatriangulane—oxaspiropentane (**3a**)—can readily be prepared by straightforward epoxidation of methylenecyclopropane.[9a–c] The alternative approach to oxaspiropentanes, especially to substituted ones, by

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Keywords: alkenes; epoxidations; heterotriangulanes; peroxides; small ring systems.

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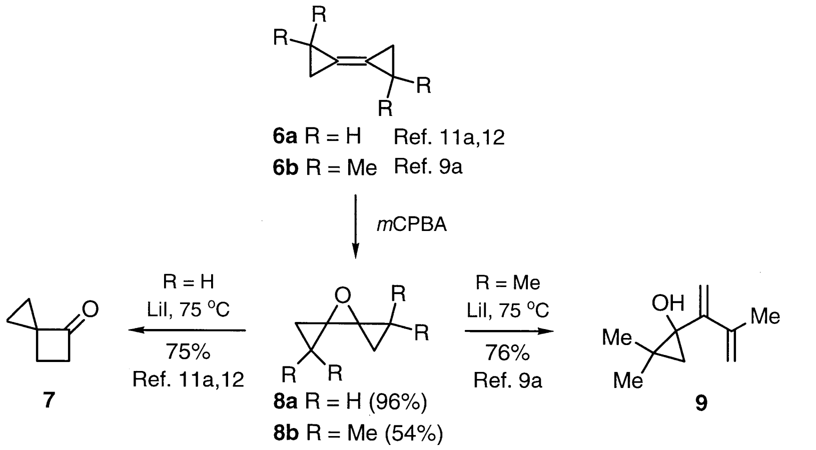


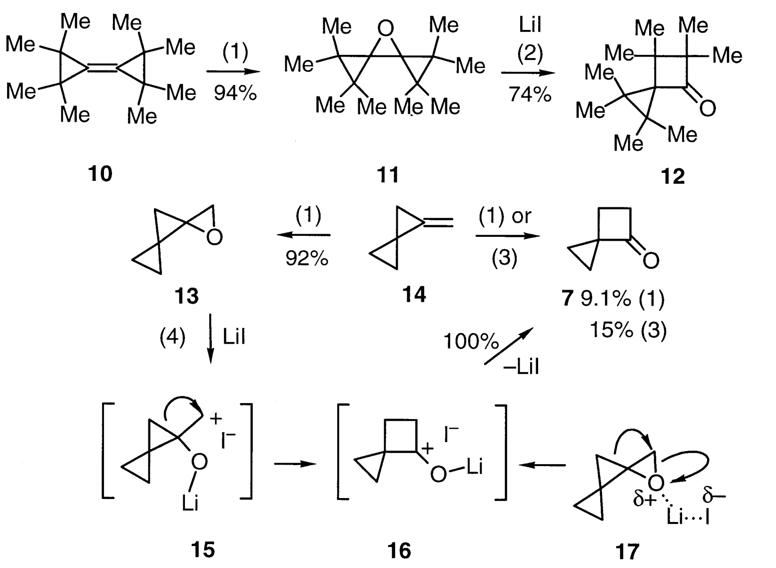
Scheme 1. Known preparations of higher oxa[*n*]triangulanes and their reactivity.

cyclopropanation of carbonyl compounds with sulfonium cyclopropylides or stabilized cyclopropylcarbanions has been exploited towards preparatively useful intermediates.[9e,f,10] The only higher oxatriangulanes that have unequivocally been characterized, are the 7-oxa[3]triangulanes **8a**,**b** which were obtained by epoxidation of bicyclopropylidene (**6a**) and its tetramethyl derivative **6b** (Scheme 1).[9a,11,12] In contrast to methylenecyclopropane, bicyclopropylidene (**6a**) reacts with *meta*-chloroperbenzoic acid (*m*CPBA) spontaneously at 0°C within 5 min.[12,13] All of the oxaspiropentanes (oxa[2]triangulanes) rapidly isomerize to cyclobutanones under the catalysis of lithium iodide and other Lewis acids, a fact which has found widespread application in organic synthesis.[9–12,14,15]

Bicyclopropylidene epoxide (**8a**), a 7-oxa[3]triangulane (7-oxadispiro[2.0.2.1]heptane) is remarkably more stable towards lithium iodide than the oxaspiropentanes, its isomerization could be effected only at 75°C.[11a,12] Under the same conditions, the sterically congested 1,1,5,5-tetramethyloxa[3]triangulane **8b** surprisingly does not yield a cyclobutanone, but instead rearranges to 2,2-dimethyl-1-(3-isoprenyl)cyclopropanol (**9**) (Scheme 1).[9a] One can only speculate that in this unique case, the ring opening of the intermediate 1-cyclopropylcyclopropyl cation to a 2-cyclopropylallyl cation is favored over the cyclopropylcarbinyl to cyclobutyl cation ring enlargement.

To start with, the possible epoxidation of permethylbicyclopropylidene (**10**),[16] which is more sterically congested than its tetramethyl analogue **8b**, was tested. Indeed, the hydrocarbon **10** did not react at all with a twofold excess of dimethyldioxirane,[17] which was chosen as an epoxidizing reagent that does not generate an acid, at room temperature within 5 h. However, the epoxidation of **10** could be achieved with *m*CPBA to furnish the permethyl-7-oxa-[3]-triangulane **11** in 94% yield (Scheme 2).

The structure of the permethyl-7-oxa[3]triangulane **11** was unequivocally established by X-ray crystal structure analysis (Fig. 1).[18] This displays the mutual repulsion of the four *endo*-oriented methyl groups, yet the sum of van der Waals radii of two nearest hydrogen atoms (2.40 Å) in two methyl groups on the different rings does not exceed the intramolecular distance (2.693 Å). Anyhow, this leads to a deformation of the oxaspiropentane units by bending (i.e. buckling of the C_2 axis which usually bisects the cyclopropane and the oxirane rings, see Fig. 1) by 16.7°



Scheme 2. (1) *m*CPBA, $NaHCO_3$, CH_2Cl_2, 0°C, 3 h; (2) C_6D_6, 100°C, 1.5 h; (3) dimethyldioxirane, acetone, 0–20°C, 2–5 h; (4) $CDCl_3$, 20°C.

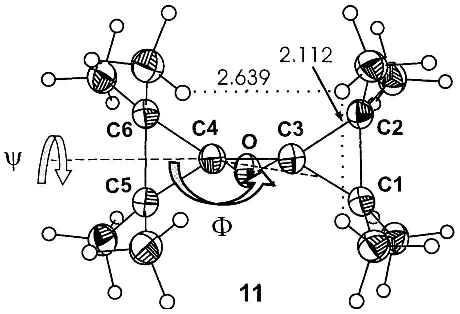
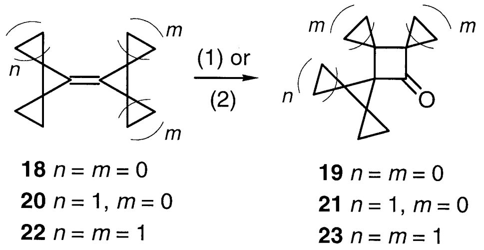


Figure 1. Molecular structure of permethyl-7-oxa[3]triangulane **11** in the crystal (selected interatomic distances are given in Å).[18]

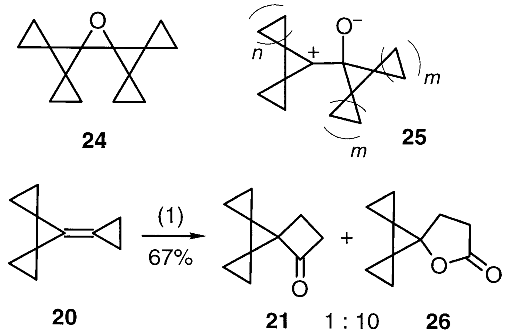
(Φ=163.3° for both moieties). This is more pronounced than even in branched [15]triangulane (Φ=168.3°).[16] However, the deformation of the oxaspiropentane units as observed for the central spiropentane units in [15]triangulane[16] by twisting (i.e. rotation of the plane of cyclopropane against that of the oxirane ring) is essentially negligible (ψ=89.4 and 89.8° for the left and right oxaspiropentane unit, see Fig. 1).

This 7-oxa[3]triangulane **11** turned out to be rather stable at 100°C as well as towards lithium iodide upon heating at 60°C in C_6D_6 solution for 0.5 h, but partially rearranged upon heating with LiI in a sealed tube at 100°C, to yield permethylspiro[2.3]hexan-4-one (**12**) (Scheme 2). The isomer of **8a**, the 1-oxa[3]triangulane **13**, at first appeared to be considerably less stable than **8a**, as an attempted epoxidation of methylenespiropentane (**14**) with either buffered *m*CPBA or dimethyldioxirane on a small scale with attempted purification by 'bulb-to-bulb' distillation (at 30°C/0.2 Torr) only gave small amounts of the known spiro[2.3]hexan-4-one (**7**)[11a,12,19] (9 and 15%, respectively) along with polymeric material. However, when performed on a larger scale (650 mg–1.6 g), epoxidation of **14** with *m*CPBA under buffered conditions did give a product which could be purified by bulb-to-bulb distillation at 0°C and 0.01 Torr in 92% yield and be assigned the structure of 1-oxa[3]triangulane **13** on the basis of its ^{1}H and ^{13}C NMR spectra (Scheme 2). Surprisingly, this product did neither undergo isomerization upon heating at 60°C in $CDCl_3$ solution, nor under flash vacuum pyrolysis conditions even at 300°C. However, addition of a catalytic quantity of lithium iodide to a solution of **13** in $CDCl_3$ at ambient temperature led to an immediate and quantitative rearrangement of **13** into **7**. Thus, the 1-oxa[3]triangulane **13** is remarkably less stable towards lithium iodide than 7-oxa[3]triangulane **8a** and even less stable than oxaspiropentane (**3a**) and its derivatives. It is most remarkable that **13** under LiI catalysis, rearranges to the same product **7** as does **8a**. For the most reasonable mechanistic interpretation one has to assume an initial opening of the distal (with respect to the spiropentane moiety) C–O bond in the oxirane ring, the resulting zwitterion **15**, which, by being a cyclopropylcarbinyl cation ought to be a reasonably stabilized species,[20] would then undergo the well-known cyclopropylcarbinyl to cyclobutyl cationic ring enlargement,[21] and the resulting intermediate **16** would liberate LiI again to yield **7** (Scheme 2). The ring enlargement of **15** to **16** proceeds regioselectively with migration of the distal bond in the spiropentane moiety of **15** only. Alternatively, the lithium iodide-complexed oxa[3]triangulane **17** could undergo a concerted ring-enlarging 1,2-migration of a proximal cyclopropyl bond in the spiropentane moiety with opening of the oxirane ring and subsequent liberation of LiI to give **7**.

Thus, one additional spirocyclopropane moiety attached to an oxaspiropentane at either end apparently does not significantly decrease the thermal stability of the corresponding oxatriangulane **8a** or **13**, respectively. However, attempted epoxidation of the mono-, bis- and tetrakis-spirocyclopropanated bicyclopropylidenes **18**, **20** and **22**[22] furnished exclusively the corresponding spirocyclopropanated



Conditions	Product and Yield (%)
(1)	**19** (59)
(2)	**19** (52)
(1)	**21** (100)
(2)	**21** (35)
(1)	**23** (97)
(2)	**23** (≤5)



Scheme 3. Attempted epoxidations of spirocyclopropanated bicyclopropylidenes **18**, **20** and **22** and further oxidation of the cyclobutanone **21**. (1) *m*CPBA, $NaHCO_3$, CH_2Cl_2, 0°C, 3 h; (2) dimethyldioxirane, acetone, 0–20°C, 2–5 h.

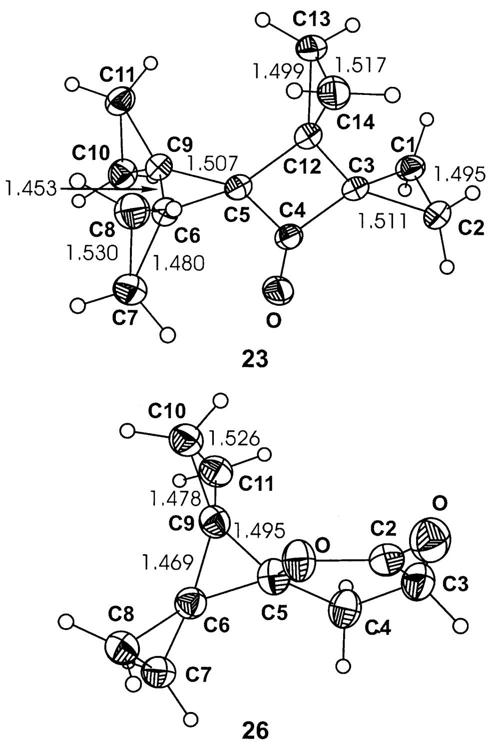


Figure 2. Molecular structures of the spirocyclopropanated cyclobutanone **23** and γ-butyrolactone **26** in the crystal (bond lengths are given in Å).[18]

cyclobutanone derivatives **19**, **21** and **23**, no matter whether buffered *m*CPBA or dimethyldioxirane was used as an oxidant (Scheme 3). This cannot be attributed to rearrangement upon purification (column chromatography), as the corresponding oxiranes could not even be detected in the NMR spectra of the crude reaction mixtures. Thus, an earlier report[8,23] on the successful preparation of the epoxide **24** from the perspirocyclopropanated bicyclopropylidene **22** was proved wrong.

In fact, the material previously obtained on a very small scale (4 mg)[23] turned out to have the same ^{1}H NMR spectroscopic data as the cyclobutanone derivative **23**, which has now been unequivocally identified (see below). Undoubtedly, the ring enlargement en route to **19**, **21** and **23** occurs at the stage of a cyclopropyl cationic intermediate of type **25**. It is noteworthy that the cationic charge preferentially develops on the cyclopropane moiety that has additional spirocyclopropane rings attached. This is due to the fact that a cyclopropyl cation is stabilized by spirocyclopropane annelation.[24] However, it is not obvious whether the intermediates **25** are formed via the corresponding oxiranes or directly from the alkene and the epoxidizing reagent.[25] Just like octamethylbicyclopropylidene (**10**), the sterically significantly less congested alkenes **20** and **22** reacted faster with *m*CPBA than with dimethyldioxirane.

With an excess of *m*CPBA, the cyclobutanone **21** rapidly undergoes a subsequent Bayer–Villiger oxidation to give the spirocyclopropanated γ-butyrolactone **26** (Scheme 3). This type of further oxidation was also observed in the reaction of the parent bicyclopropylidene (**6a**) with ozone.[11]

The structures of the spirocyclopropanated cyclobutanone **23** derived from the perspirocyclopropanated bicyclopropylidene **22** and of the γ-butyrolactone **26** were established by X-ray crystal structure analyses (Fig. 2).[18] It is interesting to compare the structural features of **23** and **26** with those of the parent cyclobutanone[26] and γ-butyrolactone.[27] The four-membered ring in **23** is almost planar with an interplanar angle of 1.6° between the planes formed by C3, C4, C5 and C3, C12, C5. This angle is significantly smaller than that in the parent cyclobutanone (19.8°), as determined by microwave and nematic phase NMR spectroscopy.[26] The γ-butyrolactone fragment in **26** is virtually as close to being planar as γ-butyrolactone itself.[27] As far as bond lengths are concerned, only the outer sphere cyclopropane rings in the [3]triangulane moieties of these molecules can be reproduced accurately enough by the previously derived general bond increment scheme for triangulanes.[28] The bond lengths in the spirocyclopropane rings attached to the four-membered ring in **23** or five-membered ring in **26** follow the rules put forward by Allen.[29] Due to the electron-withdrawing effect of the carbonyl group in **23** and carbonyloxy substituent in **26** the proximal and the distal bonds in the respective adjacent spirocyclopropane ring are lengthened and shortened, respectively.

3. Conclusion

In conclusion, one can say that for the oxa[*n*]triangulanes some sort of correlation between increasing strain of the molecules and their kinetic instability does exist. The spiroannelation of every new cyclopropane moiety to an [*n*]triangulane skeleton increases the total strain energy by at least 36.7 kcal mol^{-1},[30] but a strain-instability relationship emerges more pronouncedly in the case of oxatriangulanes **2**. Viewing it from another angle, the oxidation of oligocyclopropanated methylenecyclopropanes and bicyclopropylidenes with typical epoxidizing agents can be used as an easy access to unusual oligospirocyclopropanated cyclobutanones.

4. Experimental

4.1. General methods

Methylene chloride and acetone were purified by distillation from P_4O_{10} and K_2CO_3, respectively. Dimethyldioxirane (DMDO),[17] octamethylbicyclopropylidene (**10**),[16] methylenespiropentane (**14**),[31] cyclopropylidenespiropentane (**18**),[32] 7-cyclopropylidene-dispiro[2.0.2.1]heptane (**20**),[32] and bis(dispiro[2.0.2.1]hept-7-ylidene) (**22**),[16] were prepared according to published procedures. All other chemicals were used as commercially available (Merck, Acrõs, BASF, Bayer, Degussa AG, and Hüls AG). Organic extracts were dried with $MgSO_4$.

^{1}H and ^{13}C NMR spectra were recorded at 250 (^{1}H), and 62.9 [^{13}C, additional distortionless enhancement by polarization transfer (DEPT)] MHz with a Bruker AM 250 instrument in $CDCl_3$ soln, with residual $CHCl_3$ and $CDCl_3$, respectively, as internal reference (if not otherwise specified); δ in ppm, *J* in Hz. IR spectra were measured with a Bruker IFS 66 (FT-IR) spectrophotometer as KBr pellets or oils between KBr plates. Mass spectra (EI-70 eV and CI–NH_3) were obtained on a Finnigan MAT 95 spectrometer. Melting points were measured with a Büchi 510 capillary melting point apparatus and are uncorrected. TLC analyses were performed using Macherey–Nagel precoated sheets, 0.25 mm Sil G/UV_{254} and column chromatography using Merck silica gel, grade 60, 230–400 mesh. The CH analyses were carried out by the Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Universität Göttingen.

4.2. General procedure (GP1) for the epoxidation of alkenes 10, 14, 18, 20, and 22 with *meta*-chloroperbenzoic acid (*m*CPBA)

To a well stirred suspension of $NaHCO_3$ (1.26 g, 15 mmol) in CH_2Cl_2 (90 ml) was added the corresponding alkene (2.6 mmol) in CH_2Cl_2 (90 ml), and then a solution of *m*CPBA (0.9 equiv., 75% purity) in CH_2Cl_2 (45 ml) was added dropwise at 0°C over a period of 15 min. After stirring for an additional 1–3 h at 0°C, the mixture was poured into conc. NH_4OH aq. solution (8 ml), the inorganic layer was extracted with CH_2Cl_2 (3×20 ml), the combined organic solutions were washed with sat. NH_4Cl aq. solution (3×15 ml), dried and concentrated under reduced pressure at 0°C. The product was purified by column chromatography on silica gel.

4.3. General procedure (GP2) for the epoxidation of alkenes 10, 14, 18, 20, and 22 with dimethyldioxirane (DMDO)

To a solution of DMDO in acetone (5.76 mmol, 57.6 ml of ca. 0.1 M solution) was added the corresponding alkene (5.2 mmol) at 0°C. After stirring for an additional 2 h, the mixture was concentrated under appropriate pressure and the residue was taken up with Et_2O (30 ml), washed with water (20 ml), brine (2×20 ml), dried, concentrated under appropriate pressure at 0°C and purified by column chromatography, if not otherwise specified.

4.3.1. Spiro[2.3]heptan-4-one (7) and 1-oxadispiro[2.0.2.1]-heptane (13). (a) The crude product obtained from **14** (650 mg, 8.11 mmol), *m*CPBA (1.68 g, 7.30 mmol) and $NaHCO_3$ (3.93 g, 46.8 mmol) according to GP1 was bulb-to-bulb distilled (0°C/0.01 Torr) to give almost pure **13** (643 mg, 92%) as a colorless oil. Attempted column chromatography of 200 mg of **13** (45 g of silica gel, 25×3 cm column, pentane/Et_2O 5:1, R_f=0.23) resulted in quantitative isolation of **13**, but of the same purity. ^{1}H NMR δ: 3.33 (d, J=4.9 Hz, 1H, one of OCH_2), 3.16 (d, J=4.9 Hz, 1H, one of OCH_2), 1.48 (d, J=6.3 Hz, 1H, one of CH_2), 1.39 (d, J=6.3 Hz, 1H, one of CH_2), 1.11–0.80 (m, 4H, $2CH_2$). ^{13}C NMR δ: 57.7 (C), 48.8 (CH_2), 9.7 (CH_2), 9.2 (C), 6.8 (CH_2), 5.1 (CH_2). IR (film), cm^{-1}: 3069, 3054, 2992, 1714, 1603, 1424, 1324, 1162, 1050, 998, 970, 929, 876, 858, 824, 627, 565, 454. EI-MS *m/z*: 96 (18%, M^+), 95 (33%, M^+–H), 81 (17%, M^+–H–CH_2), 67 (86%, M^+–H–CH_2CH_2), 66 (100%, M^+–2H–CH_2CH_2), 65 (54%), 54 (60%), 53 (84%), 43 (26%), 42 (21%), 41 (42%). Heating of the solution of **13** in $CDCl_3$ (60°C, 3 h) as well as flash vacuum pyrolysis at 200 and 300°C/0.01 Torr did not result in any detectable changes in its ^{1}H and ^{13}C NMR spectra.

(b) The crude product obtained from **14** (325 mg, 4.06 mmol), *m*CPBA (839 mg, 3.65 mmol) and $NaHCO_3$ (2.52 g, 30 mmol) according to GP1, which was almost pure **13**, was bulb-to-bulb distilled at 30°C/0.2 Torr to give **7**[11a,12,18] (32 mg, 9.1%) as a colorless liquid. ^{1}H NMR δ: 3.03 (t, J=7.5 Hz, 2H, *Cbut*-CH_2), 2.22 (t, J=7.5 Hz, 2H, *Cbut*-CH_2), 1.35–1.30 (dd, J=4.3, 7.7 Hz, 2H, 2*Cpr*-H), 1.11–1.05 (dd, J=4.3, 7.7 Hz, 2H, 2*Cpr*-H). ^{13}C NMR δ: 215.5 (C), 43.8 (CH_2), 39.6 (C), 20.6 (CH_2), 16.5 ($2CH_2$).

(c) Bulb-to-bulb distillation at 30°C/0.2 Torr of the crude product obtained from **14** (163 mg, 2.03 mmol) and DMDO (2.88 mmol, 28.8 ml of a ca. 0.1 M solution in acetone) according to GP2, also furnished **7** (29 mg, 15%).

(d) To a solution of purified **13** (40 mg) in $CDCl_3$ (0.5 ml) in an NMR tube was added anhydrous lithium iodide as a powder (10 mg). Upon vigorous shaking of the tube a slightly exothermal reaction was observed. The immediately following NMR measurement indicated complete transformation of **13** into **7**.

4.3.2. 1,1,2,2,5,5,6,6-Octamethyl-7-oxadispiro[2.0.2.1]-heptane (11) and 1,1,2,2,5,5,6,6-octamethylspiro[2.3]-hexan-4-one (12). (a) The crude product mixture obtained from permethylbicyclopropylidene (**10**) (500 mg, 2.6 mmol), *m*CPBA (1.076 g, 4.68 mmol, 1.8 equiv.) and $NaHCO_3$ (1.26 g, 15 mmol) was sublimed at 100°C/0.1 Torr to give **11** (513 mg, 94%) as a colorless solid, R_f=0.33 (hexane/Et_2O 30:1), mp 94°C. ^{1}H NMR (C_6D_6) δ: 1.21 (s, 12H, $4CH_3$), 1.03 (s, 12H, $4CH_3$). ^{13}C NMR (C_6D_6) δ: 72.2 (2C), 18.1 ($4CH_3$), 17.9 (4C), 15.4 ($4CH_3$). IR (KBr), cm^{-1}: 2989, 2922, 1653, 1457, 1378, 1115, 1042, 952, 905, 766, 577, 637, 436. EI-MS *m/z*: 208 (1%, M^+), 193 (3%, M^+–CH_3), 178 (4%, M^+–$2CH_3$), 163 (2%, M^+–$3CH_3$), 125 (12%), 96 (44%), 84 (20%), 81 (100%), 69 (30%). CI-MS *m/z*: 243 (42%, M+NH_3+NH_4^+), 226 (47%, M+NH_4^+), 209 (100%, M+H^+). HRMS (EI) calcd for $C_{14}H_{24}O$ (M^+) 208.1827, found 208.1827.

(b) Heating of a solution of purified **11** (40 mg) in C_6D_6 (0.5 ml) in an NMR tube with addition of lithium iodide as a powder (10 mg) (60°C, 0.5 h) did not result in any detectable changes in its ^{1}H NMR spectrum. However, heating of this sample in a sealed tube at 100°C for 1.5 h furnished a rearranged product (74% yield) which, according to its ^{1}H and ^{13}C NMR spectra, had the structure of 1,1,2,2,5,5,6,6-octamethylspiro[2.3]hexan-4-one (**12**) (see below).

(c) A solution of epoxide **11** (131 mg, 0.63 mmol) and LiI (30 mg, 0.22 mmol) in anhydrous benzene (2 ml) was heated at 100°C for 2 h in a sealed tube. After cooling to ambient temperature, the solution was concentrated under reduced pressure. Column chromatography (120 g of silica gel, 3×35 cm column, hexane/Et_2O 30:1) gave **12** (83 mg, 63%) as a colorless solid, R_f=0.29, mp 28°C. ^{1}H NMR δ: 1.20 (s, 6H, $2CH_3$), 1.18 (s, 6H, $2CH_3$), 1.16 (s, 6H, $2CH_3$), 0.99 (s, 6H, $2CH_3$). ^{13}C NMR δ: 220.1 (C), 59.5 (C), 57.9 (C), 41.7 (C), 36.7 (2 C), 23.2 ($2CH_3$), 20.0 ($2CH_3$), 18.3

($2CH_3$), 18.0 ($2CH_3$). IR (KBr), cm^{-1}: 3011, 2926, 2869, 1750, 1557, 1379, 1162, 1100, 1040, 994. EI-MS *m/z*: 208 (38%, M^+), 193 (57%, M^+-CH_3), 165 (25%), 125 (64%), 109 (18%), 96 (100%), 84 (67%), 81 (97%), 69 (70%), 57 (20%). HRMS (EI) calcd for $C_{14}H_{24}O$ (M^+) 208.1827, found 208.1827.

4.3.3. Dispiro[3.0.2.1]octan-1-one (19). (a) Column chromatography (120 g of silica gel, 3.5×35 cm column, pentane/Et_2O 5:1) of the reaction mixture obtained from cyclopropylidenespiropentane (**18**) (276 mg, 2.60 mmol), *m*CPBA (538 mg, 2.34 mmol) and $NaHCO_3$ (1.26 g, 15 mmol) according to GP1 gave **19** (168 mg, 59%) as a colorless oil, R_f=0.45. ^{1}H NMR δ: 3.07–2.94 (ddd, *J*=6.0, 9.2, 17.5 Hz, 1H, one of *Cbut*-CH_2), 2.92–2.79 (ddd, *J*=5.7, 9.3, 17.5 Hz, 1H, one of *Cbut*-CH_2), 2.33–2.23 (ddd, *J*=5.8, 9.3, 11.2 Hz, 1H, one of *Cbut*-CH_2), 2.17–2.06 (ddd, *J*=6.0, 9.3, 11.2 Hz, 1H, one of *Cbut*-CH_2), 1.90 (d, *J*=4.0 Hz, 1H, one of *Cpr*-CH_2), 1.57 (d, *J*=4.0 Hz, 1H, one of *Cpr*-CH_2), 1.02–0.78 (m, 4H, 2*Cpr*-CH_2). ^{13}C NMR δ: 215.1 (C), 45.6 (C), 43.6 (CH_2), 25.2 (C), 23.4 (CH_2), 19.4 (CH_2), 6.2 (CH_2), 4.7 (CH_2). IR (film), cm^{-1}: 3072, 2985, 2870, 1767, 1533, 1437, 1394, 1249, 1176, 1144, 1108, 1071, 1024, 998, 956, 918, 878, 845, 828, 733. CI-MS *m/z*: 262 (5%, $2M+NH_4^+$), 157 (20%, $M+NH_3+NH_4^+$), 140 (100%, $M+NH_4^+$), 123 (5%, $M+H^+$).

(b) From **18** (552 mg, 5.20 mmol) and DMDO (5.76 mmol, 57.6 ml of a ca. 0.1 M solution in acetone) the cyclobutanone **19** (330 mg, 52%) was obtained according to GP2.

4.3.4. Trispiro[3.0.2.0.2.0]decan-1-one (21). (a) Column chromatography (50 g of silica gel, 20×2 cm column, hexane/Et_2O 5:1) of the reaction mixture obtained from 7-cyclopropylidenedispiro[2.0.2.1]heptane (**20**) (340 mg, 2.57 mmol), *m*CPBA (314 mg, 1.36 mmol) and $NaHCO_3$ (1.26 g, 15 mmol) according to GP1, gave **21** (201 mg, 100%) as a colorless solid, R_f=0.40, mp 52–54°C. ^{1}H NMR δ: 2.71 (t, *J*=7.6 Hz, 2H, *Cbut*-CH_2), 2.04 (t, *J*=7.6 Hz, 2H, *Cbut*-CH_2), 0.97–0.85 (m, 4H, 2*Cpr*-CH_2), 0.82–0.77 (m, 2H, *Cpr*-CH_2), 0.62–0.56 (m, 2H, *Cpr*-CH_2). ^{13}C NMR δ: 214.6 (C), 50.1 (C), 43.1 (CH_2), 29.4 (2C), 18.2 (CH_2), 5.8 ($2CH_2$), 4.5 ($2CH_2$). IR (KBr), cm^{-1}: 3069, 2985, 2951, 2862, 1767, 1576, 1421, 1389, 1249, 1175, 1122, 1017, 948, 867, 750, 549. EI-MS *m/z*: 148 (5%, M^+), 133 (5%), 119 (10%), 106 (18%), 105 (50%), 92 (32%), 91 (100%), 79 (35%), 77 (26%), 65 (16%), 63 (14%), 52 (18%), 51 (21%).

(b) Column chromatography (120 g of silica gel, 35×3.5 cm column, hexane/Et_2O 5:1) of the reaction mixture obtained from **20** (771 mg, 5.83 mmol) and DMDO (5.76 mmol, 57.6 ml of a ca. 0.1 M solution in acetone) according to GP2, gave **21** (302 mg, 35%).

4.3.5. Pentaspiro[2.1.0.2.0.2.0.0.2.0]tetradecan-4-one (23). (a) Column chromatography (70 g of silica gel, 20×3 cm column, hexane/Et_2O 5:1) of a reaction mixture obtained from the perspirocyclopropanated bicyclopropylidene **22** (960 mg, 5.21 mmol), *m*CPBA (1.92 mg, 8.35 mmol) and $NaHCO_3$ (2.52 g, 30 mmol) according to GP1, gave **23** (1010 mg, 97%) as a colorless solid, R_f=0.39, mp 107–108°C. ^{1}H NMR δ: 1.27–1.20 (dd, *J*=4.4, 7.7 Hz, 2H), 1.16–1.08 (ddd, *J*=4.1, 5.3, 9.4 Hz, 2H), 1.00–0.93 (ddd, *J*=4.7, 5.3, 9.5 Hz, 2H), 0.86–0.72 (m, 6H), 0.66–0.59 (ddd, *J*=4.1, 5.5, 9.3 Hz, 2H), 0.31–0.27 (dd, *J*=5.0, 6.5 Hz, 2H). ^{13}C NMR δ: 209.5 (C), 48.1 (C), 42.4 (C), 27.1 (2 C), 25.6 (C), 13.4 ($2CH_2$), 4.3 ($2CH_2$), 3.9 ($2CH_2$), 3.2 ($2CH_2$). IR (KBr), cm^{-1}: 3072, 2993, 1758, 1325, 1197, 1100, 1051, 1022, 982, 938, 876. CI-MS *m/z*: 235 (85%, $M+NH_3+NH_4^+$), 218 (100%, $M+NH_4^+$), 201 (5%, $M+H^+$).

(b) The reaction mixture obtained from **22** (980 mg, 5.32 mmol) and DMDO (20 mmol, 200 ml of a ca. 0.1 M solution in acetone) according to GP2 contained, according to its ^{1}H NMR spectrum, less than 5% of **23**.

4.3.6. 1-Oxatrispiro[4.0.2.0.2.0]undecan-2-one (26). Column chromatography (70 g of silica gel, 20×3 cm column, hexane/Et_2O 5:1) of the reaction mixture obtained from **20** (714 mg, 5.4 mmol), *m*CPBA (1.60 g, 7.0 mmol) and $NaHCO_3$ (1.26 g, 15 mmol) according to GP1, gave the cyclobutanone **21** (48 mg, 6%, R_f=0.40), and the lactone **26** (537 mg, 61%) as a colorless solid, R_f=0.20, mp 105–108°C. ^{1}H NMR δ: 2.59 (t, *J*=8.4 Hz, 2H, $COCH_2$), 2.26 (t, *J*=8.4 Hz, 2H, CH_2), 1.13–1.02 (m, 2H, *Cpr*-CH_2), 0.94–0.85 (m, 4H, 2*Cpr*-CH_2), 0.75–0.64 (m, 2H, *Cpr*-CH_2). ^{13}C NMR δ: 176.5 (C), 72.1 (C), 29.3 (CH_2), 25.2 (CH_2), 20.2 (2C), 5.8 ($2CH_2$), 5.4 ($2CH_2$). IR (KBr), cm^{-1}: 3064, 2977, 2937, 2864, 1772, 1457, 1259, 1123, 1074, 1017, 796. CI-MS *m/z*: 199 (25%, $M+NH_3+NH_4^+$), 182 (100%, $M+NH_4^+$).

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18. Crystals of compounds were grown by slow evaporation of their solutions in a mixture of Et_2O and hexane (**23** and **26**) or by sublimation at 100°C/0.1 Torr (**11**). The X-ray single crystal data were collected on a Stoe IPDS II diffractometer using graphite monochromated Mo Kα-radiation. The structure solutions and refinements on F^2 were performed with the Bruker SHELXTL program suite. The hydrogen atoms in structures **11**, **23** and **26** were located in a difference Fourier synthesis and refined isotropically. **11**: $C_{14}H_{24}O$ (208.33), monoclinic, a=16.2695(12), b=6.4521(6), c=12.5687(9) Å, β=97.406(6)°, V=1308.36(18) Å^3, Z=4, space group $P2(1)/c$, T=133(2) K, ρ=1.058 g cm^{-3}, $F(000)$=464, intensities measured: 12387 ($2\theta_{max}$=59.52°), independent: 2225 (R_{int}=0.0407), 144 parameters refined, final R indices [$I>2\sigma(I)$] $R1$=0.0352, $wR2$=0.0946, Gof=1.073, maximum and minimum residual electron density 0.208 and −0.125 e Å^{-3}. **23**: $C_{14}H_{16}O$ (200.27), monoclinic, a=12.814(3), b=7.0866(14), c=12.867(3) Å, β=109.40(3)°, V=1102.1(4) Å^3, Z=4, space group $P2(1)/c$, T=133(2) K, ρ=1.207 g cm^{-3}, $F(000)$=432, intensities measured: 3478 ($2\theta_{max}$=49.56°), independent: 1631 (R_{int}=0.0823), 136 parameters refined, final R indices [$I>2\sigma(I)$] $R1$=0.0486, $wR2$=0.1380, Gof=1.051, maximum and minimum residual electron density 0.263 and −0.212 e Å^{-3}. **26**: $C_{10}H_{12}O_2$ (164.20), triclinic, a=5.4056(11), b=7.4357(15), c=11.1700(20) Å, α=77.41(3), β=76.13(3), γ=78.23(3)°, V=419.89(15) Å^3, Z=2, space group $P-1$, T=133(2) K, ρ=1.299 g cm^{-3}, $F(000)$=176, intensities measured: 4353 ($2\theta_{max}$=49.36°), independent: 1485 (R_{int}=0.0657), 109 parameters refined, final R indices [$I>2\sigma(I)$] $R1$=0.0362, $wR2$=0.0966, Gof=1.050, maximum and minimum residual electron density 0.195 and −0.154 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited as supplementary publication no. CCDC-182317 (**11**), CCDC-182315 (**23**), and CCDC-182316 (**26**) with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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25. For example, the spiro[2.3]hexan-4-one (**7**) was formed in the reaction of bicyclopropylidene (**6a**) with ozone (67% yield) even at −78°C.[12] In this case intermediate of the type **25** was presumably formed directly from **6a** and the oxidizing agent.
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