Relative Stabilities of Spirocyclopropanated Cyclopropyl Cations

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Dispiro[2.0.2.1]hept-1-yl triflate (**3**), 7-bromo-7-phenyldispiro[2.0.2.1]heptane (**4**) and 7-chloro-7-phenylsulfanyldispiro[2.0.2.1]heptane (**6**) were prepared from bicyclopropylidene (**5**) in 50, 77 and 90% overall yield, respectively. 7-Bromo-7-cyclopropyldispiro[2.0.2.1]heptane (**8**) and 7-bromo-7-methyldispiro[2.0.2.1]heptane (**11**) were obtained by hydrobromination of 7-cyclopropylidene- (**7**) and 7-methylenedispiro[2.0.2.1]heptane (**10**) (78 and 95% yield, respectively). Methanolyses of triangulane derivatives **4**, **6**, and **8** as well as acetolysis of **6** all proceed with retention of the dispiro[2.0.2.1]heptane skeleton yielding the corresponding 7-substituted 7-methoxydispiro[2.0.2.1]heptanes **15**, **21**, and **23** as well as 7-acetoxy-7-phenylsulfanyldispiro[2.0.2.1]heptane **22** in 90, 100, 100 and 88% yield, respectively. Methanolysis of 1-bromo-1-cyclopropylcyclopropane (**24**) also gave mainly the ring-retained product **25** (66%) along with the ring-opened product **26** (33%). Apparently, an increasing number of spiro-annelated three-membered rings stabilizes a cyclopropyl cation against ring opening under solvolysis conditions. The rate of solvolysis, however, is only slightly affected by this spiroannelation, as the rate coefficient for the triflate **3** in sodium acetate-buffered methanol was determined to be $k = 3.5 \times 10^{-4}$ s^{-1} at 50 °C and 1.6×10^{-4} s^{-1} at 40 °C which is virtually the same as that for cyclopropyl triflate itself (4.02×10^{-4} s^{-1} at 70 °C in acetone/H_2O 3:2). No reaction was observed for the bromotriangulane **11** in pure methanol, and solvolysis of **11** in aqueous methanol only led to products **27**–**30** which were formed by ring-enlarging and ring-opening rearrangements of the initially formed 7-dispiro[2.0.2.1]heptyl cation.

Introduction

The influence of different substituents upon the stability of a cyclopropyl cation has been studied in great detail.[1] The ring opening of the parent cyclopropyl to the allyl cation is known to proceed virtually without a measurable activation energy.[1a] The latter, however, can be significantly higher for appropriately substituted cyclopropyl cations. A rather efficient stabilization at least towards ring opening may, apparently, be achieved by one or two spiro-annelated cyclopropane rings, as was corroborated by the recently determined kinetics[2] for the bromination of various methylenetriangulanes and cyclopropylidenetriangulanes.[3] However, the intermediate cation in an alkene bromination reaction is always — but not to the same degree — influenced by the β-bromo substituent, and this influence can only be deduced from computations which may leave some uncertainty as to the real structure of the intermediate cations. More direct evidence may be extracted from kinetic and product studies of solvolysis reactions of appropriate spirocyclopropanated derivatives (*cf.* ref.[1]). So far, such studies have been carried out only for spiropentane derivatives accurately enough with respect to their mechanisms and the structures of the respective intermediates. Thus, the kinetic data for the solvolysis of spiropentyl chloride versus cyclopropyl chloride ($k = 7.1 \times 10^{-5}$ s^{-1} versus $k = 1.4 \times 10^{-5}$ s^{-1})[4] indicated that the spiro-annelated three-membered ring increases the rate only by a factor of five, whereas an α-cyclopropyl substituent usually accelerates a solvolysis reaction by factors of between 10^5 and 10^7.[1a] Moreover, a ring expansion and ring opening were the predominant transformation modes in solvolysis reactions of spiropentane derivatives.[5,6] More recently, we have undertaken a solvolysis study of various 7-substituted dispiro[2.0.2.1]heptane ([3]triangulane) derivatives, and the results of this study are reported here.

Results and Discussion

The dispiro[2.0.2.1]heptyl derivatives **3**, **4**, **6**, **8**, and **11** were essentially all prepared starting from the readily available bicyclopropylidene (**5**)[7] (Scheme 1).

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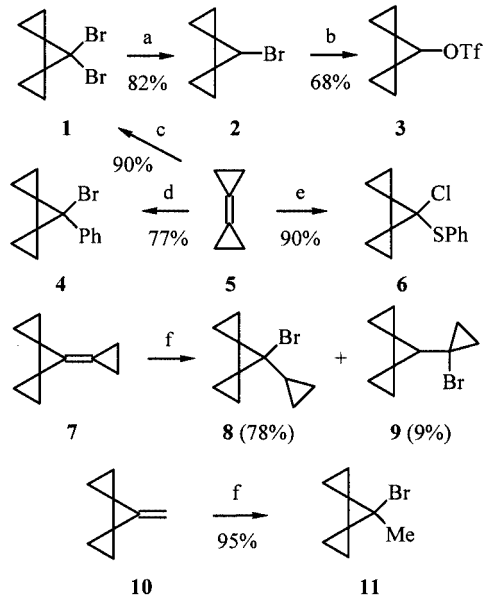


Scheme 1. Preparation of 7-(trifluoromethylsulfonyloxy)[3]triangulane **3** and 7,7-disubstituted dispiro[2.0.2.1]heptanes ([3]triangulanes) **4**, **6**, **8** and **11**: a) Bu_3SnH, Et_2O, 25 °C, 3 h; b) (1) *t*BuLi, THF, −78 °C, 2 h; (2) O_2, −78 °C, 1 h; (3) Tf_2O, −90→20 °C; c) $CHBr_3$, KOH (powder), TEBACl, CH_2Cl_2, 0→20 °C, 5 h; d) $PhCHBr_2$, *t*BuOK, pentane, 20 °C, 48 h; e) $PhSCHCl_2$, 50% NaOH, CH_2Cl_2, 20 °C, 48 h; f) HBr, pentane, −30 °C

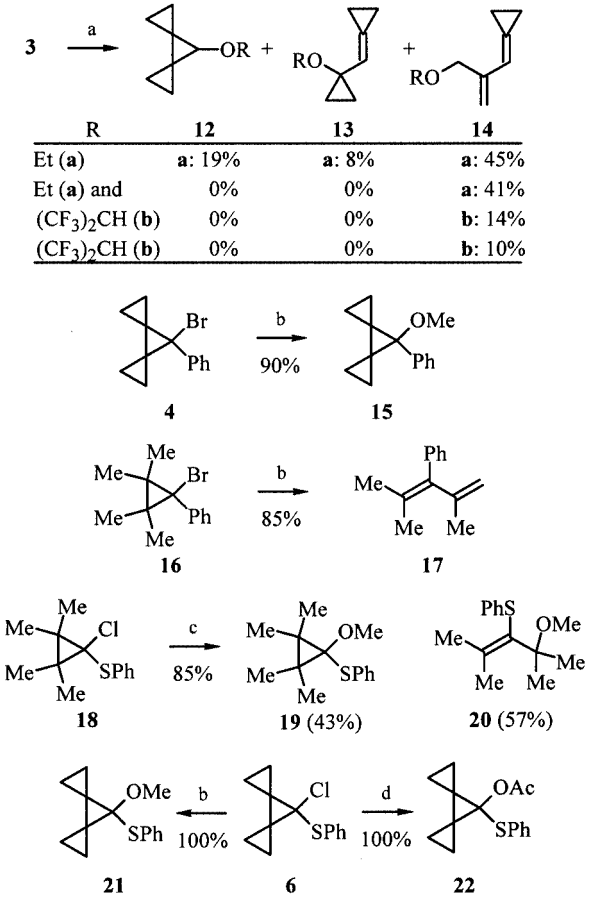
The dispiro[2.0.2.1]hept-7-yl triflate (**3**) could not be obtained along the route developed by Applequist for the preparation of spiropentyl triflate[5] [addition of chloro(2-chloroethoxy)carbene onto **5** followed by deprotection with PhLi and esterification with Tf_2O], as the lithium alkoxide of 7-hydroxidispiro[2.0.2.1]heptane turned out to be rather unstable (*cf.* ref.[8]). However, reductive monodebromination of the dibromocarbene adduct **1** of bicyclopropylidene[9] with tributyltin hydride gave the corresponding monobromide **2**, which cleanly underwent bromine-lithium exchange upon treatment with *tert*-butyllithium at low temperature (−78 °C). Subsequent reaction with oxygen and trapping of the intermediate lithium dispiro[2.0.2.1]hept-7-yl oxide with triflic anhydride at low temperature gave the triflate **3** in 56% overall yield (Scheme 1). The addition of bromo(phenyl)carbene[10] and chloro(phenylsulfanyl)carbene[11] to **5** furnished 7-bromo-7-phenyl- (**4**) and 7-bromo-7-(phenylsulfanyl)[3]triangulane (**6**) in 77 and 90% yield, respectively. Hydrobromination of 7-cyclopropylidene[3]triangulane (**7**) and 7-methylene[3]triangulane (**10**), which were prepared in three and two steps, respectively, from bicyclopropylidene (**5**),[3,12] gave 7-bromo-7-cyclopropyl[3]triangulane (**8**; 78% yield) along with its regioisomer **9** (9% yield) and 7-bromo-7-methyl[3]triangulane (**11**; 95% yield), respectively (Scheme 1).

The products from the solvolysis of the triflate **3** in ethanol (buffered with sodium acetate) were mainly the allyl ethers **13a** (8%) and **14a** (45%) arising from single and twofold ring opening of the intermediate cation, respectively, along with 19% of the ring-retained dispiroheptyl ethyl ether **12a**. For comparison, the triflate **3** was also solvolyzed in hexafluoro-2-propanol, which is known for its low nucleophilicity, in the presence of 2,6-lutidine, and also in a 1.9:10 mixture of ethanol and hexafluoro-2-propanol. In these cases, only the esters **14a** and **14b** arising from twofold ring opening of the intermediate 7-dispiro[2.0.2.1]heptyl cation were isolated (Scheme 2). Although the proportion of the product **12a** in which all three cyclopropane rings had been retained was relatively small (19%), the hydrolysis of spiropentyl triflate gave an even smaller amount of the ring-retained product (5%).[5] The rate of solvolysis of the triflate **3** in sodium acetate-buffered methanol was determined to be $k = 3.5 \times 10^{-4}$ s^{-1} at 50 °C and 1.6×10^{-4} s^{-1} at 40 °C (see Exp. Sect.). In comparison to the rate for cyclopropyl triflate itself (4.02×10^{-4} s^{-1} at 70 °C in acetone/H_2O 3:2[13]) that of **3** is only two times higher when adjusted to the same solvent (80% EtOH) and temperature (70 °C). This is in line with Applequist's observation for spiropentyl chloride.[4] Each additional spirocyclopropane ring accelerates the solvolysis reaction only by a factor of 1.4 to 5. It is also consistent with the observation that the bromine additions to methylenetriangulanes and cyclopropylidenetriangulanes proceed essentially with the same rate as those to the corresponding oligomethyl-substituted ethylenes.[2] However, the proportions of ring-retained and ring-opened products from cyclopropyl and spiropentyl chloride as well as dispiro[2.0.2.1]heptyl triflate **3** ranged from 0% for cyclopropyl and spiropentyl chloride[14] to 19% for **3** (Scheme 2). On the other hand, 2,2,3,3-tetramethyl-1-phenylcyclopropyl bromide (**16**) upon solvolysis in methanol at 65 °C underwent complete ring opening to yield only the 1,3-butadiene derivative **17** without incorporation of a methoxy group (*cf.* ref.[20] in[1c]) (Scheme 2).

With its rather well carbocation-stabilizing α-phenyl group, the bromotriangulane **4** undergoes methanolysis with complete retention of the dispiro[2.0.2.1]heptane skeleton to yield the methoxy derivative **15** (90% isolated). For comparison, hydrolysis of 1-phenylspiropentyl bromide has been reported to also proceed with 92% retention of the spiropentyl moiety at 25 °C.[5]

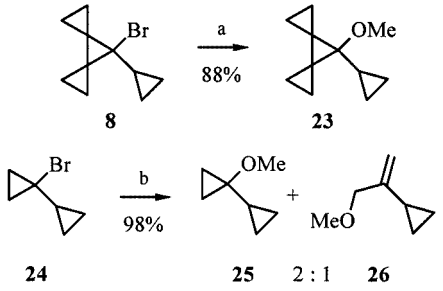
The cation-stabilizing effect of a phenylsulfanyl group is known to be particularly powerful,[1,11b] and in agreement with this the methanolysis as well as acetolysis of 7-phenylsulfanyldispiro[2.0.2.1]hept-7-yl chloride (**6**) proceeded very smoothly with complete retention of the triangulane skeleton in the products **21** and **22** (Scheme 2). Even upon attempted recrystallization from methanol, **6** was completely solvolyzed to **21**. For comparison, methanolysis of 1-chloro-1-(phenylsulfanyl)-2,2,3,3-tetramethylcyclopropane (**18**) under these conditions has been reported to proceed with only 43% conservation of the cyclopropane ring (Scheme 2).[11b]

An α-cyclopropyl group is known to have the largest stabilizing effect of any α-alkyl substituent on a carbocation,[1] and methanolysis of 7-bromo-7-cyclopropyldispiro[2.0.2.1]-heptane (**8**) accordingly proceeded without ring opening to yield only the methyl ether **23** (88% isolated) (Scheme 3). This demonstrates that the two spirocyclopropane groups in **8** significantly contribute to the — at least kinetic — stability of the intermediate cyclopropyl cation, since 1-



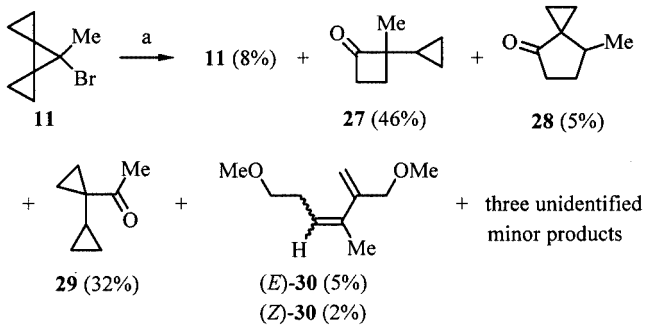
Scheme 2. Products of alcoholysis of triflate **3** and of solvolyses of various [3]triangulane derivatives **4**, **6**, and their tetramethylcyclopropane analogues **16**, **18**: a) EtOH, NaOAc and/or $(CF_3)_2CHOH$, 2,6-lutidine, 40 °C, 1 h; b) MeOH, 65 °C, 10 min−24 h; c) MeOH, MeONa (2 equiv.), 80 °C, 2 h; d) HOAc, NaOAc, 110 °C, 1 h

bromo-1-cyclopropylcyclopropane (**24**)[12,15] undergoes methanolysis to give both the ring-retained **25** and the ring-opened product **26** in 98% yield with a ratio of 2:1 (Scheme 3).



Scheme 3. Methanolysis of 7-bromo[3]triangulane (**8**) and 1-bromo-1-cyclopropylcyclopropane (**24**): a) MeOH, 65 °C, 30 min; b) MeOH, 65 °C, 14 days

Contrary to this, the methyl-substituted analogue of **8**,7-bromo-7-methyl[3]triangulane (**11**) remained unchanged after heating in refluxing methanol for 14 days. Heating of **11** at 65 °C in aqueous methanol (1:2) did result in solvolysis, however a set of three ketones **27**−**29** along with two diastereomeric dimethoxy-substituted dienes (*E*)- and (*Z*)-**30** was formed (Scheme 4).



Scheme 4. Solvolysis of 7-bromo-7-methyl[3]triangulane (**11**): a) MeOH/H_2O, 2:1, 65 °C, 74 h

Since the ketones **27** and **28** have similar spectroscopic characteristics and identical molecular masses, the structure of the known compound **27**[16] was rigorously proved by an X-ray crystal structure analysis of its tosylhydrazone **31** (Figure 1A). There are two crystallographically independent molecules of **31**[17] in the unit cell, one of which is disordered over two positions with distinctively different orientations of the cyclopropyl group. Both molecules have similar conformations of the tosylhydrazone moiety with torsional angles N−S−C−C = −66.1(2)° as well as 77.4(2)° and N−N−S−C = −54.4(2)° as well as 60.2(2)°, which are typical for arylsulfonamides.[18a] The orientations of the cyclopropyl group relative to the cyclobutane ring is different in the independent molecules of **31** (Figure 1B) and can be described by torsional angles τ (C3···C1−C6-center of C7−C8 bond) of −66.6°, −54.6° and 56.7°. Interestingly, there are only two other structures in the CCDC data file in which a cyclopropylcyclobutane moiety is not part of a three-dimensional framework.[18b] Both of these structures contain a number of bulky substituents on the four-membered ring, and two out of three cyclopropyl groups in these compounds adopt an *s-trans*-conformation with a τ angle of about 180°. These examples imply almost unhindered rotation around the C−C bond between two cycles. The independent molecules of **31** in the unit cell form dimers, connected by pairs of N−H···O hydrogen bonds with N···O distances of 2.968(3) and 2.991(3) Å, respectively (Figure 1A). In the packing of these dimers in the crystal (Figure 1C), a number of weak CH···O(N) interactions play a significant role.

Among the solvolysis products **27**−**30**, only the dimethoxy-substituted butadienes (*E*)- and (*Z*)-**30** (7% total) may have been formed by initial cyclopropyl to allyl cation ring opening of the intermediate **35** (Scheme 5). Most probably, ketones **27**−**29** resulted by acid-catalyzed rearrangements of the intermediate protonated alcohols **33** and **38**. Protonation of **33** at the quaternary carbon C7 with opening

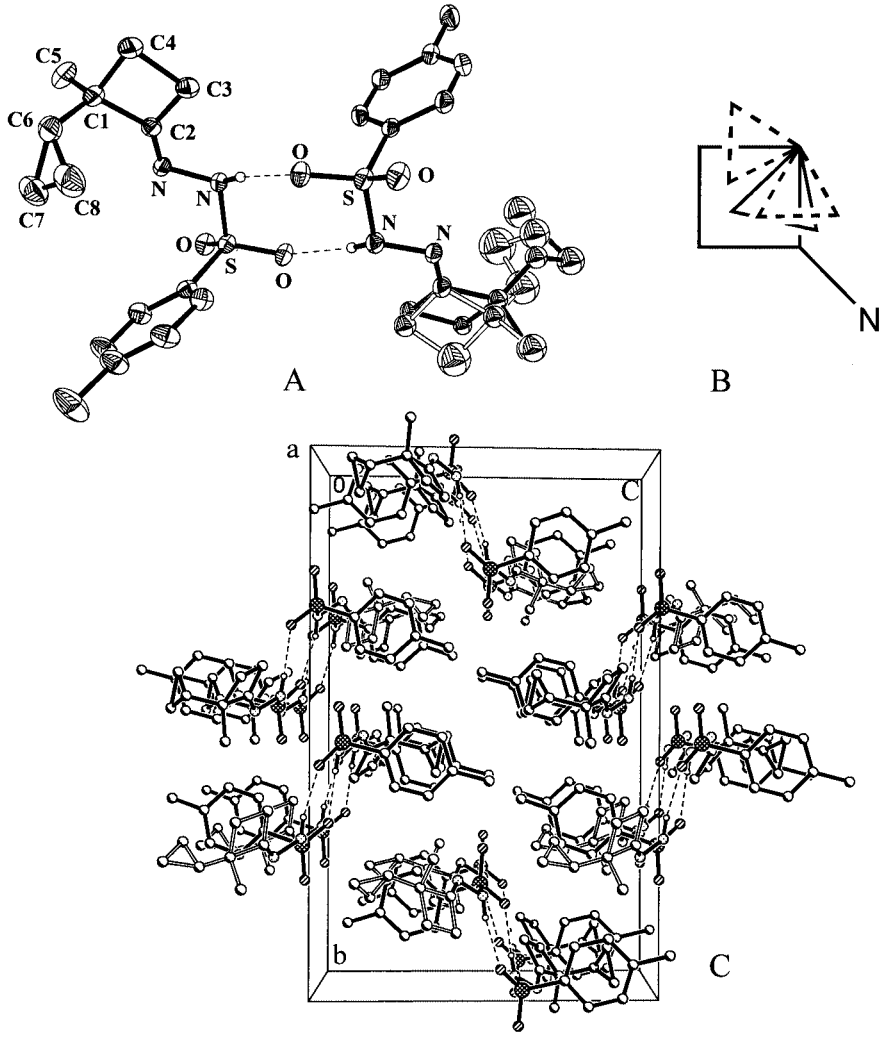


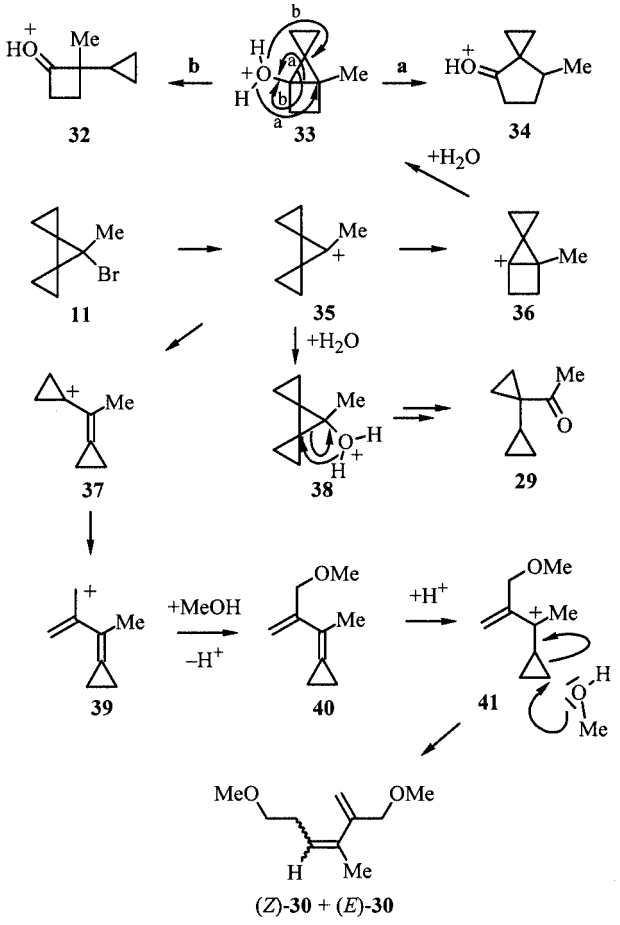
Figure 1. Molecular structure of the tosylhydrazone of 2-cyclopropyl-2-methylcyclobutanone (**31**) in the crystal (A), schematic representation of three conformations of cyclopropylcyclobutane fragment in **31** (B) and crystal packing of **31** (C)[17]

of the bridgehead-bridgehead bond leads to **34**, the protonated form of ketone **28** (mode a), whereas protonation of **33** at the spirocarbon yields **32**, the protonated major ketone **27** (mode b). Such acid-catalyzed ring-opening rearrangements of cyclopropanols are well documented.[19] The protonated cyclopropanols **38** and **33**, in turn, must have been formed by nucleophilic attack of water on the initially formed carbocation **35** and the bicyclopentyl bridgehead cation **36**, respectively. Quite remarkably, the latter would have originated from the former by the well-known ring-enlarging cyclopropylmethyl to cyclobutyl cation rearrangement.[20,21] The intermediate protonated alcohols **33** and **38** may also have been formed by nucleophilic attack of the water solvent on the bicyclobutonium-type cation common to both **35** and **36**, but from different sides.[20a]

Unfortunately, nothing is known about solvolysis reactions of bicyclo[2.1.0]pentyl and/or bicyclo[3.1.0]hexyl derivatives with a leaving group at the bridgehead position.

Conclusion

The carbocations generated from cyclopropyl substrates have been classified in three categories:[1a] (1) open planar structures arising from concerted ionization and ring opening, (2) half-opened, and (3) closed structures. The latter two are non-planar and result whenever the disrotatory ring opening is retarded or prevented for reasons of steric congestion or increasing ring strain. The cations arising from 7-dispiro[2.0.2.1]heptyl derivatives apparently belong to the second two types, depending on the nature of the additional substituent in the 7-position. Even the kinetically stabilizing effect of the two α-spirocyclopropane rings, which does not significantly influence the rate of solvolysis, in most cases causes the solvolysis products to be formed without ring opening. The intermediate from **8** actually is a particular tricyclopropylmethyl cation, one in which two of the cyclopropyl groups are rigidly held in a bisected orientation, but with a drastically decreased bonding angle which causes ad-



Scheme 5. Mechanistic rationalization for the formation of compounds **27**–**30**

ditional angle strain in the central three-membered ring. The accumulated experimental evidence leads one to arrange the variously substituted and spirocyclopropanated cyclopropyl cations according to their relative stabilities as shown in Figure 2.

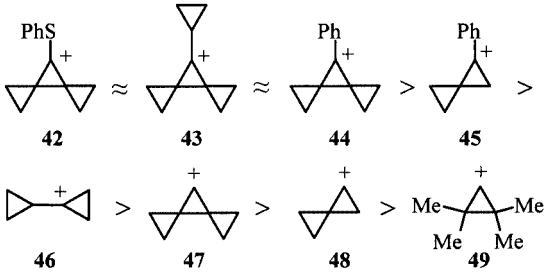
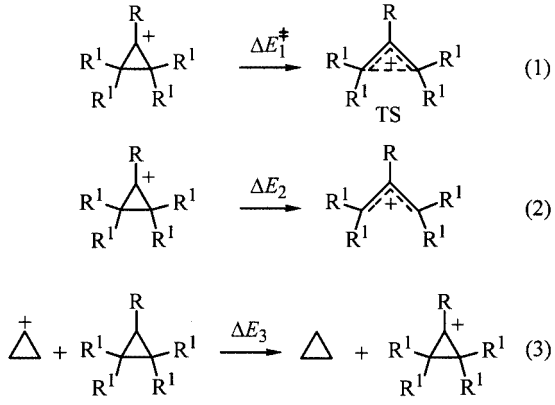


Figure 2. The apparent relative kinetic stabilities of variously substituted and spirocyclopropanated cyclopropyl cations

This experimentally derived stability sequence was probed by computations. All structures were optimized at the B3LYP/6-31G(d,p) level of theory. Vibrational frequency calculations at this level of theory were used to characterize each of the stationary points as either a minimum (zero imaginary frequencies) or transition state (one imaginary frequency). Single point energies were calculated at the MP2/6-311+G(2d,p) level of theory at the optimized B3LYP/6-31G(d,p) geometries. All calculations were performed with the Gaussian 98 package of programs.[22] All energy values are calculated at the MP2/6-311+G(2d,p)// B3LYP/6-31G(d,p) level of theory and are given in kcal mol^{-1}.



The results are shown in Figure 3, where $\Delta E_1^{\ddagger}$ values are the ring-opening barriers according to Equation (1), ΔE_2 values are the thermodynamic driving forces for ring opening according to Equation (2), and ΔE_3 values are the thermodynamic stabilities in the gas phase according to the isodesmic Equation (3). Positive values of ΔE_2 indicate that this cyclopropyl cation is thermodynamically more stable than the corresponding allyl cation.

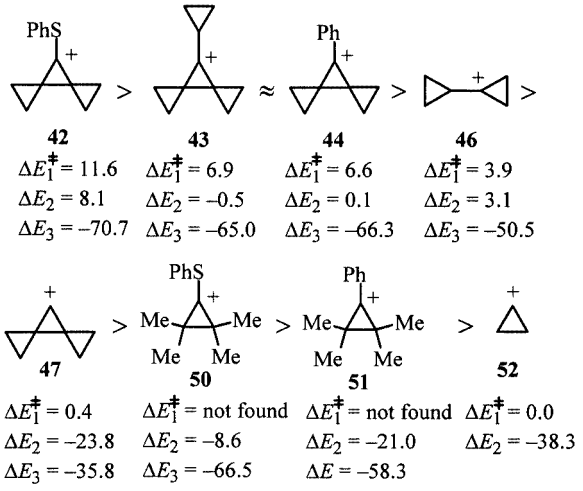


Figure 3. Relative kinetic and thermodynamic stabilities of variously substituted and spirocyclopropanated cyclopropyl cations according to MP2/6-311+G(2d,p)//B3LYP/6-31G(d,p) calculations (all values in kcal·mol^{-1}); the parent cyclopropyl cation **52** is not a minimum but a transition structure connecting two equivalent forms of the corresponding allyl cation

The computed barrier for the ring opening of the cyclopropyl ring, which leads to the kinetic stability order of the cations **42**–**47**, **50**, **51**, corresponds very nicely to the experimentally derived one, based on the product distribution between ring-retaining products and ring-opened products. The calculated high barrier for the ring opening of cation **42** should make this the most stable kinetically, and this

was really observed experimentally. However, the results for cyclopropyl cation **46** are not in line with its chemical behavior under solvolytic conditions (see Scheme 3). We believe that this can be attributed to solvation effects which are not included in the calculations, as the latter simulate the situation in the gas phase only. The 7-dispiro-[2.0.2.1]heptyl cation (**47**) is rather unstable thermodynamically, yet the small positive value of $\Delta H^{\neq}$ in such cations (0.4 kcal mol^{-1} in the case of **47**) presumably causes the unusual reactivity of the bromide **11** upon solvolysis (Schemes 4, 5).

It is interesting to note that the energy differences between the cyclic and the ring-opened cations, ΔE_2, which denote the thermodynamic driving force for ring opening, do not correspond to the barriers for ring opening and therefore cannot be used to predict the kinetic stabilities towards ring opening of substituted cyclopropyl cations. This is yet another case where the Hammond postulate is misleading.

Experimental Section

General: ^{1}H and ^{13}C NMR: Spectra were recorded at 250 (^{1}H), and 62.9 [^{13}C, additional DEPT (Distortionless Enhancement by Polarization Transfer)] MHz on Bruker AM 250 instrument in $CDCl_3$ soln, $CHCl_3/CDCl_3$ as internal reference; δ in ppm, *J* in Hz. IR: Perkin−Elmer 298. FT-IR: Bruker IFS 66, measured as KBr pellets, oils between KBr plates. MS (EI): Finnigan MAT 95 spectrometer (70 eV). M. p.: Büchi 510 capillary melting point apparatus, uncorrected. GC analyses: Siemens Sichromat 1−4, 25 m capillary column CP-SIL-5-CB, if not otherwise specified. GC separations: Intersmat 130 instrument, 20% SE-30 on Chromaton W−AW−DMCS, 2000 × 8.2 mm Teflon column. TLC: Macherey−Nagel precoated sheets, 0.25 mm Sil G/UV$_{254}$. Column chromatography: Merck silica gel, grade 60, 230−400 mesh. Starting materials: Anhydrous diethyl ether and THF were obtained by distillation from sodium benzophenone ketyl, methanol and ethanol from magnesium alkoxides, and dichloromethane from P_4O_{10}. Pentane was shaken with conc. sulfuric acid for 12 h, then with a 0.5 N solution of $KMnO_4$ in 3 M H_2SO_4 for 24 h, washed with diluted aq. solution of oxalic acid, aq. 5% $NaHCO_3$ solution, dried ($MgSO_4$) and distilled from P_4O_{10}. 7,7-Dibromodispiro-[2.0.2.1]heptane (**1**),[9a] bicyclopropylidene (**5**),[12,15] 7-cyclopropylidene-dispiro[2.0.2.1]heptane (**7**),[12] 7-methylenedispiro-[2.0.2.1]heptane (**10**),[23] 1-bromo-1-phenyl-2,2,3,3-tetramethylcyclopropane (**16**),[10a] 1-bromo-1-cyclopropylcyclopropane (**24**),[12,15] and dichloromethylphenyl sulfide[24] were prepared according to the published procedure. All other chemicals were used as commercially available (Merck, Acrõs, BASF, Bayer, Hoechst, Degussa AG, and Hüls AG). All reactions were performed under argon. Organic extracts were dried with $MgSO_4$.

Preparation of the Substrates for Solvolysis

7-Bromodispiro[2.0.2.1]heptane (2): Bu_3SnH (46.3 g, 42.8 mL, 159 mmol) was added dropwise within 3 h to a stirred solution of the dibromide **1** (40.0 g, 159 mmol) in anhydrous Et_2O (100 mL) maintaining the temperature at 20−25 °C inside the flask. The reaction mixture was "bulb-to-bulb" distilled into a cold (−78 °C) trap under reduced pressure (0.1 Torr), and the content of the trap was distilled under reduced pressure to give **2** (22.6 g, 82%) as a colorless liquid, b.p. 81 °C (8 Torr). ^{1}H NMR: δ = 0.75−0.85 (m, 2 H, CH_2), 0.86−1.02 (m, 4 H, 2 CH_2), 1.07−1.20 (m, 2 H, CH_2), 3.65 (s, 1 H, CHBr) ppm. ^{13}C NMR: δ = 6.9, 8.6 (2 CH_2), 32.8 (CH), 21.6 (2 C) ppm. MS (EI), *m*/*z* (%) = 93 (21) [M^+ − Br], 92 (15), 91 (100) [$C_7H_7^+$], 66 (7), 65 (32) [$C_5H_5^+$]. C_7H_9Br (173.05): calcd. C 48.58, H 5.24, Br 46.18; found C 48.77, H 5.41, Br 46.11.

7-(Trifluoromethanesulfonyloxy)dispiro[2.0.2.1]heptane (3): A 1.8 M solution of *t*BuLi in pentane (14.2 mL, 25.6 mmol) was added dropwise at −78 °C within 1.5 h to a stirred solution of the bromide **2** (4.0 g, 23.11 mmol) in anhydrous THF (100 mL). After stirring for an additional 30 min, a strong stream of dry oxygen was passed through the reaction mixture at this temp. for 1 h. The mixture was stirred for an additional 30 min, cooled to −90 °C, and trifluoromethanesulfonic anhydride (6.51 g, 3.78 mL, 23.07 mmol) was added slowly. The mixture was allowed to warm to ambient temperature, poured into ice-cold water (200 mL) and quickly extracted with Et_2O (3 × 100 mL). The combined organic extracts were washed with sat. aq. NH_4Cl solution (3 × 50 mL), water and brine (50 mL each), dried and concentrated under reduced pressure. The residue was purified by flash column chromatography (100 g of silica gel, 35 × 4 cm column, pentane) to give **3** (3.84 g, 68%) as a colorless oil, R_f = 0.70. ^{1}H NMR: δ = 0.82−0.97 (m, 4 H, 2 CH_2), 1.10−1.25 (m, 4 H, 2 CH_2), 4.85 (s, 1 H, CHOTf) ppm. ^{13}C NMR: δ = 5.2, 7.1 (2 CH_2), 71.4 (CH), 18.4 (2 C), 118.6 (q, *J* = 320 Hz, CF_3) ppm. ^{19}F NMR: δ = 87.5 ppm. MS (EI), *m*/*z* (%) = 91 (100) [$C_7H_7^+$], 81 (75), 79 (80), 69 (90), 53 (100). $C_8H_9F_3O_3S$ (242.22): calcd. C 39.67, H 3.75; found C 39.89, H 3.89.

7-Bromo-7-phenyldispiro[2.0.2.1]heptane (4): A solution of α,α-dibromotoluene (4.25 g, 2.81 mL, 17.0 mmol) in pentane (10 mL) at 0 °C was added dropwise within 1 h to a suspension of *t*BuOK (4.0 g, 35.6 mmol) in anhydrous pentane (30 mL) containing bicyclopropylidene (**5**) (3.0 g, 3.51 mL, 37.4 mmol). The resulting mixture was vigorously stirred at ambient temperature over a period of 2 days, then diluted with pentane (100 mL), filtered through a pad of celite (20 g) and concentrated under reduced pressure. Column chromatography of the residue (130 g of silica gel, 30 × 5 cm column, pentane) gave **4** (3.26 g, 77%) as a colorless oil, R_f = 0.60. ^{1}H NMR: δ = 1.03−1.12 (m, 4 H, 2 CH_2), 1.20−1.27 (m, 4 H, 2 CH_2), 7.21−7.47 (m, 5 H, C_6H_5) ppm. ^{13}C NMR: δ = 9.4, 9.6 (2 CH_2), 127.5, 128.0 (2 CH), 126.9 (CH), 29.9 (2 C), 48.1, 141.3 (C) ppm. MS (EI), *m*/*z* (%) = 250/248 (0.5/0.5) [M^+], 222/220 (4/4) [$M^+ - C_2H_4$], 221/219 (2.5/2.5) [$M^+ - C_2H_5$], 171 (37), 169 (50) [M^+ − Br], 154 (34), 141 (100) [M^+ − Br − C_2H_4], 115 (40), 91 (20) [$C_7H_7^+$]. MS (HR-EI): 248.0200 ($C_{13}H_{13}Br$, calcd. 248.0200). $C_{13}H_{13}Br$ (249.14): calcd. C 62.67, H 5.26; found C 62.44, H 5.30.

7-Chloro-7-(phenylsulfanyl)dispiro[2.0.2.1]heptane (6): A 50% NaOH solution (80 mL) was added slowly at 0 °C to a vigorously stirred solution of bicyclopropylidene (**5**; 8.01 g, 9.38 mL, 100 mmol), TEBACl (500 mg) and dichloromethylphenyl sulfide (14.0 g, 72.5 mmol) in dichloromethane (100 mL), and the reaction mixture was vigorously stirred at ambient temperature for an additional 2 days. After the phases had separated, the inorganic phase was extracted with CH_2Cl_2 (2 × 100 mL), the combined organic phases were washed with sat. NH_4Cl solution (2 × 50 mL), water and brine (100 mL each), dried and concentrated under reduced pressure. As the product was neither stable towards silica gel nor towards heating, the residue was dissolved in pentane (100 mL), cooled to −30 °C overnight and quickly filtered to give **6** (15.4 g, 90%) as yellow crystals, m.p. 72 °C. IR (KBr): $\tilde{\nu}$ = 3064 cm^{-1}, 2987, 1582, 1571, 1477, 1440, 1413, 1024, 1009, 802, 744, 689. ^{1}H NMR: δ = 0.89−0.95 (m, 4 H, 2 CH_2), 1.12−1.25 (m, 4 H, 2 CH_2),

7.05−7.25 (m, 5 H, C_6H_5) ppm. ^{13}C NMR: δ = 7.7, 8.0 (2 CH_2), 127.8, 128.8 (2 CH), 126.2 (CH), 31.0 (2 C), 57.0, 134.3 (C) ppm. MS (EI), *m*/*z* (%) = 238/236 (7/20) [M^+], 201 (11) [$M^+ - Cl$], 168 (3), 167 (11), 161/159 (33/100) [$M^+ - C_6H_5$], 129/127 (5/14) [$M^+ - SC_6H_5$], 123 (21), 109 (10), 91 (46) [$C_7H_7^+$]. $C_{13}H_{13}ClS$ (236.75): calcd. C 65.95, H 5.53, Cl 14.97; found C 65.82, H 5.72, Cl 15.09.

7-Bromo-7-cyclopropyldispiro[2.0.2.1]heptane (8) and 7-(1′-Bromocyclo-propyl)dispiro[2.0.2.1]heptane (9): A 0.3 M solution of HBr in pentane (10 mL, 3 mmol) was added at −30 °C over 30 min to a stirred solution of 7-cyclopropylidenedispiro[2.0.2.1]heptane (**7**) (200 mg, 1.51 mmol) in olefin- and water-free pentane (50 mL). The reaction mixture was stirred at −30 °C for 1 h, and then treated with $NaHCO_3$ (500 mg) at this temp. After 30 min of additional stirring, the mixture was poured into an ice-cold 5% $NaHCO_3$ solution (50 mL), and the water layer was extracted with pentane (2 × 50 mL). The combined organic phases were washed with brine before they were dried and concentrated under reduced pressure to give 280 mg (87%) of **8** and **9** as a 9.6:1 mixture that could not be separated because compounds **8**, **9** are unstable towards silica gel.
8: ^{1}H NMR: δ = 0.46−0.53 (m, 2 H, CH_2), 0.54−0.60 (m, 2 H, CH_2), 0.76−0.83 (m, 2 H, CH_2), 0.84−0.90 (m, 2 H, CH_2), 0.92−0.98 (m, 2 H, CH_2), 1.12−1.19 (m, 2 H, CH_2), 1.37−1.45 (m, 1 H, CH) ppm. ^{13}C NMR: δ = 4.78, 7.81, 7.83 (2 CH_2), 25.21 (CH), 19.62 (2 C), 51.73 (C) ppm. IR (film): $\tilde{\nu}$ = 2940 cm^{-1}, 2860, 2800, 1015, 820, 770, 750, 635. GC-MS (EI), *m*/*z* (%) = 213/211 (0.3/0.3) [$M^+ - H$], 131 (9) [$M^+ - H - HBr$], 117 (34), 105 (83) [$M^+ - Br - C_2H_4$], 79 (33), 69 (100).
9: ^{1}H NMR: δ = 0.45−0.61 (m, 4 H, 2 CH_2), 0.75−0.97 (m, 6 H, 3 CH_2), 1.12−1.19 (m, 2 H, CH_2), 1.32−1.47 (m, 1 H, CH) ppm. ^{13}C NMR: δ = 7.82 (4 CH_2), 4.71 (2 CH_2), 25.25 (CH), 19.59 (2 C), 51.60 (C) ppm.

7-Bromo-7-methyldispiro[2.0.2.1]heptane (11): Hydrogen bromide (2.29 g, 28.26 mmol) was condensed at −78 °C into a stirred solution of 7-methylenedispiro[2.0.2.1]heptane (**10**) (2.00 g, 18.84 mmol) in anhydrous pentane (40 mL). The reaction mixture was warmed to −30 °C over a period of 30 min, stirred for an additional 30 min at this temp., poured into ice-cold sat. aq. $NaHCO_3$ solution (200 mL) and then extracted with pentane (2 × 50 mL). The combined organic extracts were washed with brine (50 mL), dried and concentrated under reduced pressure. The residue was distilled under reduced pressure to give **11** (3.35 g, 95%) as a colorless liquid, b.p. 40 °C (0.5 Torr), which solidified upon standing at 0 °C, m.p. 28−29 °C. ^{1}H NMR: δ = 0.74−0.81 (m, 2 H, CH_2), 0.82−1.11 (m, 6 H, 3 CH_2), 1.73 (s, 3 H, CH_3) ppm. ^{13}C NMR: δ = 7.1, 8.6 (2 CH_2), 27.0 (CH_3), 26.8 (2 C), 44.1 (C) ppm. $C_8H_{11}Br$ (187.08): calcd. C 51.36, H 5.93, Br 42.71; found C 51.27, H 5.76, Br 42.56.

General Procedure 1 (GP1) for the Methanolysis of Compounds 3, 4, 6, 8, 11, 16, 24: A solution of the substrate (6 mmol) in anhydrous methanol (20 mL) was heated under reflux with GC monitoring for the indicated time. After completion of the reaction, the mixture was poured into an ice-cold solution of $NaHCO_3$ (10 g) in water (100 mL) and extracted with Et_2O (3 × 50 mL). The combined organic extracts were washed with brine (50 mL), dried and concentrated under reduced pressure. The residue was purified as described below.

Solvolysis of the Triflate 3. a) In Ethanol: A mixture of **3** (1.210 g, 5 mmol), NaOAc (575 mg, 7 mmol) and anhydrous ethanol (10 mL) was stirred at 40 °C with GC monitoring. After 1 h, the mixture was worked up according to GP1. The residue was "bulb-to-bulb" distilled at 20 °C into a cold (−78 °C) trap under reduced pressure (0.1 Torr). The content of the trap (500 mg, 72%), according to its ^{1}H NMR spectrum, was a mixture of 7-ethoxydispiro-[2.0.2.1]heptane (**12a**), [(1′-ethoxycyclopropyl)methylene]cyclopropane (**13a**) and 3-cyclopropylidene-2-(ethoxymethyl)propene (**14a**) in a 2.38:1:5.63 ratio. The pure samples were obtained by preparative GC.
12a: ^{1}H NMR: δ = 0.61−0.69 (m, 2 H, CH_2), 0.69−0.78 (m, 2 H, CH_2), 0.87−0.95 (m, 2 H, CH_2), 0.99−1.08 (m, 2 H, CH_2), 1.19 (t, *J* = 7.0 Hz, 3 H, CH_3), 3.55 (q, *J* = 7.0 Hz, 2 H CH_2), 3.65 (s, 1 H, CH) ppm. ^{13}C NMR: δ = 15.3 (CH_3), 3.6, 6.1 (2 CH_2), 65.8 (CH_2), 62.2 (CH), 18.6 (2 C) ppm.
13a: ^{1}H NMR: δ = 0.74−0.81 (m, 2 H, CH_2), 0.93−1.02 (m, 4 H, 2 CH_2), 1.09−1.18 (m, 2 H, CH_2), 1.16 (t, *J* = 7.0 Hz, 3 H, CH_3), 3.51 (q, *J* = 7.0 Hz, 2 H CH_2), 5.89 (br. s, 1 H, =CH) ppm. ^{13}C NMR: δ = 15.5 (CH_3), 13.6 (2 CH_2), 0.5, 2.9, 63.0 (CH_2), 119.3 (CH), 63.21, 120.6 (C) ppm.
14a: ^{1}H NMR: δ = 1.04−1.12 (m, 2 H, CH_2), 1.18−1.28 (m, 2 H, CH_2), 1.22 (t, *J* = 7.0 Hz, 3 H, CH_3), 3.53 (q, *J* = 7.0 Hz, 2 H CH_2), 4.22 (s, 2 H OCH_2), 5.16 (br. s, 1 H, $=CH_2$) 5.22 (br. s, 1 H, $=CH_2$), 6.45 (s, 1 H, =CH) ppm. ^{13}C NMR: δ = 15.2 (CH_3), 1.2, 4.5, 66.0, 71.0, 113.9 (CH_2), 118.1 (CH), 124.1, 143.3 (C) ppm.
b) In Hexafluoro-2-propanol: From a mixture of **3** (750 mg, 3.1 mmol), 2,6-lutidine (750 mg, 0.82 mL, 7 mmol), hexafluoro-2-propanol (5 mL) and water (0.15 mL), 3-cyclopropylidene-2-[(hexafluoroisopropyloxy)methyl]propene (**14b**) (81 mg, 10%) was obtained under the conditions of the preceding experiment after preparative GC separation: ^{1}H NMR: δ = 1.05−1.15 (m, 2 H, CH_2), 1.17−1.32 (m, 2 H, CH_2), 4.18 (sept, *J* = 6.25 Hz, 1 H, OCH), 4.59 (s, 2 H OCH_2), 5.29 (br. s, 1 H, $=CH_2$) 5.33 (br. s, 1 H, $=CH_2$), 6.45 (s, 1 H, =CH) ppm. ^{13}C NMR: δ = 122.5 (d, *J* = 295.6 Hz, 2 CF_3), 1.0, 5.4, 74.1, 117.8 (CH_2), 118.1 (CH), 126.5, 143.3 (C) ppm.
c) In a Hexafluoro-2-propanol/Ethanol Mixture: From a mixture of **3** (1.00 g, 4.13 mmol), 2,6-lutidine (643 mg, 0.70 mL, 6 mmol), EtOH (1.50 g, 1.91 mL, 32.6 mmol) and hexafluoro2-propanol (10 mL), compounds **14b** (yield 14%) and **14a** (yield 41%) were obtained under the conditions of the preceding experiment after 2 h of stirring at 25 °C. The yields were determined from the ^{1}H NMR spectrum of the mixture obtained after "bulb-to-bulb" distillation.

7-Methoxy-7-phenyldispiro[2.0.2.1]heptane (15): The reaction mixture obtained from **4** (1.58 g, 6.34 mmol) after 24 h at reflux temperature according to GP1, was purified by flash column chromatography (60 g of silica gel, 35 × 3 cm column, pentane/Et_2O 40:1) to give **15** (1.14 g, 90%) as a colorless oil, R_f = 0.30. ^{1}H NMR: δ = 0.68−0.90 (m, 4 H, 2 CH_2), 0.90−1.01 (m, 2 H, CH_2), 1.26−1.37 (m, 2 H, CH_2), 3.45 (s, 3 H, OMe), 7.14−7.24 (m, 1 H, C_6H_5), 7.29−7.38 (m, 4 H, C_6H_5) ppm. ^{13}C NMR: δ = 55.4 (CH_3), 5.8, 6.0 (2 CH_2), 125.9 (3 CH), 127.8 (2 CH), 26.4 (2 C), 67.9, 140.3 (C) ppm. MS (EI), *m*/*z* (%) = 199 (60) [$M^+ - H$], 185 (100) [$M^+ - CH_3$], 171 (230) [$M^+ - C_2H_4 - H$], 157 (50) [$M^+ - COCH_3$], 128 (45), 115 (30) [$M^+ - COC_4H_9$], 105 (38), 91 (20) [$C_7H_7^+$], 77 (60) [$C_6H_5^+$].

2,4-Dimethyl-3-phenylpenta-1,3-diene (17): The residue (1.16 g, 85%) obtained from 1-bromo-1-phenyl-2,2,3,3-tetramethylcyclopropane (**16**) (2.00 g, 7.90 mmol) after 24 h under reflux according to GP1 consisted of essentially pure **17** as revealed by its spectroscopic data.[25]

7-Methoxy-7-(phenylsulfanyl)dispiro[2.0.2.1]heptane (21): The reaction mixture obtained from **6** (1.50 g, 6.34 mmol) after 10 min under reflux according to GP1 was taken up in methanol and cooled to −60 °C. The precipitate was quickly filtered off to give **21**

(1.46 g, 99%) as a colorless solid, m.p. 66 °C. ^{1}H NMR: δ = 0.69−0.73 (m, 2 H, CH_2), 0.88−0.92 (m, 2 H, CH_2), 0.96−1.01 (m, 2 H, CH_2), 1.26−1.30 (m, 2 H, CH_2), 3.45 (s, 3 H, OMe), 7.11−7.14 (m, 1 H, C_6H_5), 7.20−7.29 (m, 4 H, C_6H_5) ppm. ^{13}C NMR: δ = 54.2 (CH_3), 5.69, 5.74 (2 CH_2), 127.6, 128.6 (2 CH), 125.3 (CH), 27.3 (2 C), 73.7, 135.8 (C) ppm. MS (EI), *m/z* (%) = 231 (6) [$M^+ - H$], 217 (11) [$M^+ - CH_3$], 155 (100) [$M^+ - C_6H_5$], 123 (13), 91 (14) [$C_7H_7^+$]. $C_{14}H_{16}OS$ (232.33): calcd. C 72.37, H 6.94; found C 72.47, H 7.05.

7-Cyclopropyl-7-methoxydispiro[2.0.2.1]heptane (23): The residue (0.416 g, 88%) obtained from **8** (0.614 g, 2.88 mmol) after 30 min under reflux according to GP1 consisted of essentially pure **23** as revealed by its spectroscopic data. ^{1}H NMR: δ = 0.33−0.42 (m, 2 H, CH_2), 0.45−0.70 (m, 6 H, 3 CH_2), 0.80−0.90 (m, 2 H, CH_2), 0.95−1.05 (m, 2 H, CH_2), 1.12−1.25 (m, 1 H, CH), 3.42 (s, 3 H, OMe) ppm. ^{13}C NMR: δ = 54.5 (CH_3), 2.0, 3.6, 4.9 (2 CH_2), 12.0 (CH), 21.1 (2 C), 66.5 (C) ppm.

7-Acetoxy-7-(phenylsulfanyl)dispiro[2.0.2.1]heptane (22): Compound **6** (1.50 g, 6.34 mmol) was added in one portion to a stirred mixture of acetic acid (3.0 g, 2.86 mL, 50 mmol) and sodium acetate (4.10 g, 50 mmol) at 110 °C. After stirring for an additional 1 h, the mixture was cooled to ambient temperature, poured into ice-cold water (100 mL) and worked up according to GP1 but with Et_2O extraction. The residue was recrystallized from pentane at −30 °C to give 1.62 g (100%) of **22** as a colorless solid. An analytical sample was obtained by crystallization from MeOH/H_2O. M.p. 76 °C. ^{1}H NMR: δ = 0.72−0.76 (m, 2 H, CH_2), 0.80−0.84 (m, 2 H, CH_2), 1.04−1.08 (m, 2 H, CH_2), 1.16−1.20 (m, 2 H, CH_2), 2.12 (s, 3 H, CH_3), 7.13−7.18 (m, 1 H, C_6H_5), 7.22−7.27 (m, 4 H, C_6H_5) ppm. ^{13}C NMR: δ = 21.3 (CH_3), 5.8, 6.5 (2 CH_2), 127.6, 128.7 (2 CH), 125.7 (CH), 27.4 (2 C), 68.9, 135.6, 169.7 (C) ppm. $C_{15}H_{16}O_2S$ (260.33): calcd. C 69.20, H 6.20; found C 69.04, H 6.03.

Methanolysis of 7-Bromo-7-methyldispiro[2.0.2.1]heptane (11): From the residue (922 mg), which was obtained from **11** (1.182 g, 6.32 mmol) after stirring for 74 h at 65 °C in a mixture of MeOH and H_2O (2:1, 24 mL) according to GP1, 2-cyclopropyl-2-methylcyclobutanone (**27**; 359 mg, 46%), 7-methylspiro[2.4]heptan-4-one (**28**; 38 mg, 5%), 1-(bicyclopropyl-1-yl)ethanone (**29**; 252 mg, 32%), (*Z*)-6-methoxy-2-(methoxymethyl)hexa-1,3-diene [(*Z*)-**30**; 24 mg, 2%] and (*E*)-6-methoxy-2-(methoxymethyl)hexa-1,3-diene [(*E*)-**30**; 55 mg, 5%] along with 98 mg (8%) of the starting material **11** were isolated by column chromatography (40 g of silica gel, 30 × 2 cm column, pentane/Et_2O 10:1.5). **11**: R_f = 0.67.

27:[16] Oil, R_f = 0.42. ^{1}H NMR: δ = 0.01−0.14 (m, 1 H, CH_2), 0.27−0.32 (m, 1 H, CH_2), 0.33−0.44 (m, 2 H, CH_2), 0.81−0.85 (m, 1 H, CH), 1.17 (s, 3 H, CH_3), 1.56−1.65 (m, 2 H, CH_2), 2.79−2.85 (m, 2 H, CH_2) ppm. ^{13}C NMR: δ = 21.2 (CH_3), 1.0, 1.2, 21.9, 42.4 (CH_2), 15.6 (CH), 64.0, 214.5 (C) ppm.

28: Oil, R_f = 0.38. ^{1}H NMR: δ = 0.37−0.45 (m, 2 H, CH_2), 0.79−0.85 (m, 2 H, CH_2), 1.26 (d, *J* = 7.2 Hz, 3 H, CH_3), 1.58−1.71 (m, 2 H, CH_2), 2.81−2.90 (m, 3 H, CH_2, CH) ppm. ^{13}C NMR: δ = 21.5 (CH_3), 4.3, 4.9, 23.9, 42.0 (CH_2), 19.1 (CH), 69.5, 209.4 (C) ppm. $C_8H_{12}O$ (124.18): calcd. C 77.37, H 9.74; found C 77.18, H 9.81.

29: Oil, R_f = 0.25. ^{1}H NMR: δ = −0.05 to −0.02 (m, 2 H, CH_2), 0.41−0.55 (m, 4 H, 2 CH_2), 0.93−0.97 (m, 2 H, CH_2), 1.31−1.42 (m, 1 H, CH), 2.25 (s, 3 H, CH_3) ppm. ^{13}C NMR: δ = 27.6 (CH_3), 3.2, 14.6 (2 CH_2), 11.9 (CH), 32.0, 210.5 (C) ppm. $C_8H_{12}O$ (124.18): calcd. C 77.37, H 9.74; found C 77.25, H 9.69.

E-**30:** Oil, R_f = 0.17. ^{1}H NMR: δ = 1.80 (s, 3 H, CH_3), 2.32−2.46 (m, 2 H, CH_2), 3.31 (s, 3 H, OCH_3), 3.33 (s, 3 H, OCH_3), 3.38 (s, 2 H, OCH_2), 3.43 (t, *J* = 7.0 Hz, 2 H, OCH_2), 5.11 (s, 1 H, =CH_2), 5.16 (s, 1 H, =CH_2), 5.61 (t, *J* = 7.0 Hz, 1 H, =CH) ppm. ^{13}C NMR: δ = 14.1, 57.9, 58.6 (CH_3), 29.1, 72.0, 73.9, 112.7 (CH_2), 123.9 (CH), 134.2, 145.0 (C) ppm.

Z-**30:** Oil, R_f = 0.08. ^{1}H NMR: δ = 1.82 (s, 3 H, CH_3), 2.33−2.48 (m, 2 H, CH_2), 3.29 (s, 3 H, OCH_3), 3.30 (s, 3 H, OCH_3), 3.35 (s, 2 H, OCH_2), 3.45 (t, *J* = 7.1 Hz, 2 H, OCH_2), 5.05 (s, 1 H, =CH_2), 5.10 (s, 1 H, =CH_2), 5.71 (t, *J* = 7.1 Hz, 1 H, =CH) ppm. ^{13}C NMR: δ = 10.8, 55.8, 58.5 (CH_3), 27.1, 71.1, 71.9, 113.6 (CH_2), 123.9 (CH), 133.1, 146.1 (C) ppm.

Tosylhydrazone of 2-Cyclopropyl-2-methylcyclobutanone (31): Ketone **27** (200 mg, 1.61 mmol) was added to a solution of tosylhydrazine (300 mg, 1.61 mmol) in hot methanol (3 mL), and the resulting mixture was kept at 0 °C overnight. The precipitate was collected on a filter to give **31** (407 mg, 86%) as a white powder, m.p. 130−131 °C. ^{1}H NMR: δ = −0.20 to −0.15 (m, 1 H, CH_2), 0.16−0.27 (m, 3 H, CH_2), 0.77−0.87 (m, 1 H, CH), 1.21 (s, 3 H, CH_3), 1.54−1.78 (m, 2 H, CH_2), 2.43 (s, 3 H, CH_3), 2.48−2.65 (m, 2 H, CH_2), 7.25 (s, 1 H, NH), 7.35 (d, *J* = 6.3 Hz, 2 H, Ar-H), 7.79 (d, *J* = 6.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 21.6, 23.2 (CH_3), 0.9, 1.2, 26.0, 27.4 (CH_2), 127.8, 129.5 (2 CH), 17.9 (CH), 51.7, 135.1, 143.9, 166.0 (C) ppm.

Determination of Rate Constants for the Methanolysis of 3: The solvolysis reaction of **3** was monitored by ^{19}F NMR spectroscopy[26] using a Varian VXR 500 instrument. A solution of **3** (10 mg) and NaOAc (20 mg) in a mixture of methanol (0.6 mL) and [D_4]methanol (10 μL) was thermostatted within 5 min, and ^{19}F NMR spectra were recorded every 5 min. The rate constants were determined by integration of the ^{19}F signals for the starting material (δ = 88.40 ppm with C_6F_6 as internal standard) and the trifluoromethylsulfonate anion (Δ_δ = 3.25 ppm). The determined values were equal to $k = 3.5 \times 10^{-4}$ s^{-1} at 50 °C and 1.6×10^{-4} s^{-1} at 40 °C.

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[17] The crystals of **31** were obtained by slow evaporation of its solution in hexane/Et_2O. The X-ray data were collected at 120.0 K on a Bruker SMART CCD 1 K diffractometer [λ(Mo-K_α), graphite monochromator, ω-scan, 0.3°/frame] equipped with an Oxford Cryostream LT-device. At 120.0(2) K crystal of **31** ($C_{15}H_{20}N_2O_2S$, M = 292.39, crystal size 0.22 × 0.20 × 0.11 mm^3) is monoclinic, a = 9.6680(3), b = 22.6816(8), c = 14.3919(5) Å, β = 93.51(2)°, V = 3150.0(2) $Å^3$, Z = 8, space group $P2_1/c$, ρ = 1.233 Mg/m^3. A total of 27025 intensities were measured: (θ_{max} = 27.5°), yielding 7232 independent reflections (R_{int} = 0.0525). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 for all data. Non-hydrogen atoms (except the disordered ones) were refined with anisotropic displacement parameters, H-atoms were placed in calculated positions and refined in "riding mode", H-atoms of amino groups were refined isotropically. Final $R1$ = 0.0627 for 362 refined parameters and 5042 reflections with $I \geq 2\sigma(I)$, $wR2$ (all data) = 0.1887, GOF = 1.062, maximum and minimum residual electron density 0.833 (in the vicinity of disordered atoms of one of the independent molecules) and −0.472 e·Å−3. CCDC-214664 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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