Reactivities of Methylenetriangulanes and Spirocyclopropanated Bicyclopropylidenes toward Bromine. Relative Stabilities of Spirocyclopropanated versus Methyl-Substituted Bromonium Ions

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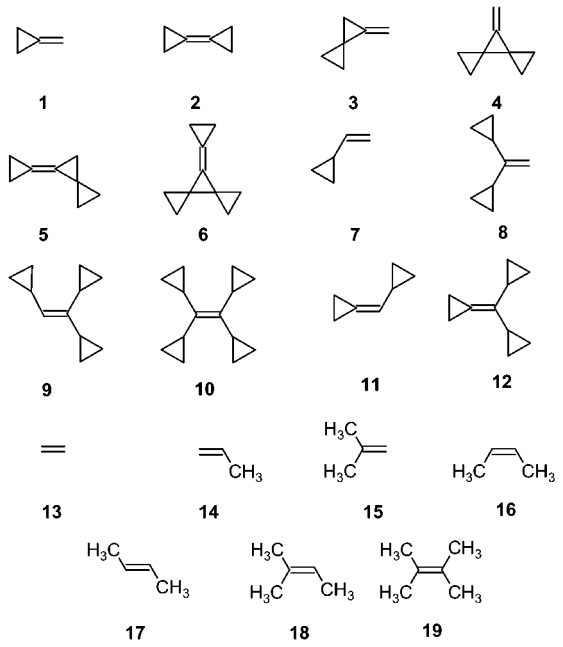
The bromine additions to methylenecyclopropane (**1**), bicyclopropylidene (**2**), and spirocyclopropanated methylenecyclopropanes and bicyclopropylidenes **3**−**6** in methanol at 25 °C proceed essentially with the same rate as those to the corresponding oligomethyl-substituted ethylenes. An increasing number of spiroannelated three-membered rings enhances the rate of bromination and stabilizes the intermediate cyclopropyl bromonium cations against ring opening in the course of bromine addition. Calculations at the B3LYP/6-311G(d,p) level show that unsymmetrical bromonium ions are the intermediates, and that they are stabilized by the spiroannelation with cyclopropane rings. The bromonium ion derived from **1** is less stable by 6.3 kcal mol^{-1} than that from isobutene. One or two spirocyclopropane rings as in **3** and **4** stabilize the corresponding bromonium ion by 9.6 and 16.4 kcal mol^{-1}, respectively, while one or two α-cyclopropyl substituents as in ethenylcyclopropane (**7**) and 1,1-dicyclopropylethene (**8**) stabilize the corresponding bromonium ions by 13 and 29 kcal mol^{-1}, respectively. The experimental bromination rates of all the studied alkenes correlate reasonably well ($r^2 = 0.93$) with calculated relative energies of the corresponding bromonium ions. The correlation is even better within the series of methylenecyclopropanes **1**, **3**, and **4** ($r^2 = 0.974$) and bicyclopropylidenes **2**, **5**, and **6** ($r^2 = 0.999$). The experimental bromination rates also correlate fairly well with the first ionization energies of the corresponding alkenes **1**−**12** (with $r^2 = 0.963$) and **13**−**19** (with $r^2 = 0.991$). The calculated preferred nucleophilic attack of a water molecule at both the C$^{1'}$ and C^1 atoms of representative bromonium ions conforms well to the experimentally observed product distribution.

Introduction

Understanding the influence of strain in organic molecules upon their reactivity is of fundamental importance for theoretical as well as experimental studies. Methylenecyclopropane (**1**), bicyclopropylidene (**2**), and their spirocyclopropanated analogues **3**−**6** are among the most highly strained alkenes and thus exhibit an enhanced reactivity toward a wide range of electrophiles and cyclophiles. A correlation of their reactivities with their inherent strain would therefore be of special interest. A large variety of chemical transformations have been performed with hydrocarbons **1**[1] and **2**;[2] e.g., cycloadditions to compounds **3**−**6** were used as key steps in the preparation of linear and branched triangulanes.[3]



However, one of the simplest reactions[4]—the electrophilic addition of halogens onto the double bond—has

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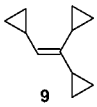
never been investigated for this family of hydrocarbons, at least not with respect to its quantitative implications (qualitative results for **1**[5a−f] and substituted methylenecyclopropanes[5g−p] have been reported). Electrophilic halogenations of alkenes are some of the classical reactions in organic chemistry, and their mechanisms are well documented by various investigations on kinetics and products.[6] Comparison of the steric and electronic effects caused by substitution at the doubly bonded carbon atoms of various alkenes were carried out by independent rate studies of chlorination,[7] bromination,[8] and iodination.[9] In bromination, the steric effects were found to be smaller than electronic effects, regardless of the degree of substitution at the double bond.[8,10] In contrast to the great amount of experimental work devoted to this reaction, theoretical studies especially on the nature of chloronium[11] and bromonium ions[12] are scarce.

Table 1. Rate Coefficients (k_{Br_2}) for the Addition of Bromine to Hydrocarbons 1−6, 9, and 12 in Methanol at 25 °C and First Ionization Energies (IEs) of 1−6, 9, and 12 as Taken from He(I) Photoelectron Spectra (PES)

Alkene	k_{Br_2} [mol^{-1} L s^{-1}]	log k_{Br_2}	$Q = k_{Br_2}/k_{Br_3^-}$	IE [eV]	Ref.
 **1**	(3.66±0.09)×10^2	2.56	17	9.57	15
 **2**	(4.70±0.05)×10^4	4.6	29	8.93	16
 **3**	(5.90±0.27)×10^3	3.77	26	9.10	17
 **4**	(1.95±0.10)×10^5	5.29	26	–[a]	17
 **5**	(1.63±0.04)×10^6	6.21	24	8.70	17
 **6**	(3.42±0.11)×10^7	7.53	55	8.50	18
 **9**	(3.0±2.0)×10^8	8.48	24	7.48	19
 **12**	(8.0±2.00)×10^8	8.90	9	8.25	20

[a] Due to serious overlapping of bands the PES of **4** is not readily interpretable.

To quantify the nucleophilicities of the double bonds in **1**−**6**, we have investigated experimentally the rates of bromine addition and have evaluated computationally the relative stabilities of the respective intermediate bromonium ions. For comparison, the cyclopropyl-substituted alkenes **9** and **12** also have been probed. The products of all these reactions were characterized to reveal the relative stabilities of the intermediate cations as a function of the number and position of spiroannelated or attached cyclopropyl groups.

Results and Discussion

Bromination Rate Coefficients. Kinetic Effects of Spiroannelated and Attached Cyclopropyl Groups. The rate coefficients, k_{Br_2}, of free bromine addition to alkenes **1**−**6**, **9**, and **12** (Table 1) were measured in methanol by following bromine uptake spectrophotometrically[13] for rate coefficients smaller than 10^5 mol^{-1}

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Table 2. Rate Coefficients (k_{Br_2}) for the Addition of Bromine to Ethylene and Methyl-Substituted Ethylenes in Methanol at 25 °C and First IEs of the Alkenes as Taken from He(I) PES

Olefin	k_{Br_2} [mol^{-1} L s^{-1}]	log k_{Br_2}[a]	Q[a]	IE [eV][b]
13[c]	4.65	0.67	20	
14	4.03×10^2	2.61	20	9.73
15	3.72×10^4	4.57	30	9.24
16	2.38×10^4	4.38	15	9.12
18	1.29×10^6	6.11	39	8.68
19	1.24×10^7	7.09	27	8.27

[a] From ref 21. $Q = k_{Br_2}/k_{Br_3^-}$. [b] From ref 22. [c] From ref 23.

L s^{-1} and amperometrically[14] in the higher reactivity range (Table 1). Methanol has been chosen as the reaction medium since numerous kinetic data for the bromination of a large variety of ethylenic compounds are at present available in this solvent.[6b,21] A comparison of the new rate data for cyclopropanated methylenecyclopropanes with those of approximately analogously methyl-substituted ethylenes (Table 2)[21] shows that the reactivity ranges of the two series of alkenes are rather similar and spread over a range of roughly 6 orders of magnitude. This contrasts with the correlation between the rate of bromination and the number of methyl groups in methylated ethylenes. Thus, the nucleophilicity of the double bond in **1** closely resembles that of propene; the reactivity of **2** is very close to that of isobutene (**15**) or 2-butene (**16**), and the bis(spirocyclopropane)-annelated bicyclopropylidene **6** reacts approximately at the same rate as tetramethylethylene (**19**). Accordingly, the activating effect of a three-membered ring geminally linked to a double bond is similar to that of a single methyl substituent.

The influence of cyclopropyl substituents attached to the double bond as in alkenes **9** and **12** is more significant as shown by the bromination rate of **12**, which is close to the diffusion control limit (5×10^9 mol^{-1} L s^{-1}).[24]

The successive spirocyclopropanation of the three-membered rings in **1** and **2** leads to significant accelerations of the bromination for compounds **3**−**6**, despite a certain increase in steric congestion.[2,25] The kinetic effects of the spiroannelated cyclopropane rings are roughly additive. On going from **1** to **3**, the rate increases by a factor of 16, and on going to **4** the second spirocyclopropane group causes an additional rate increase by a factor of 33. The same effect is observed in the bicyclopropylidene series **2**, **5**, and **6** in which the acceleration factors are 35 and 21 successively. These additivities show unambiguously that there is no steric retardation due to the spiroannelated cyclopropane groups. The effects of these spiroannelations are markedly smaller than the mean effect of a methyl group (factor of 60) in the series of methylated ethylenes. The effect of a cyclopropyl substituent as in **9** and **12** is completely different, with a drastic acceleration of 2×10^6 being observed when two cyclopropyl groups are attached to **1**, and tricyclopropylethylene (**9**) reacts slightly more slowly than **12**.

The rate coefficients in Tables 1 and 2 were measured in the presence of several different bromide ion concentrations (2×10^{-2} to 2×10^{-1} M) and extrapolated to $[Br^-] = 0$. Under these conditions, two brominating species, free bromine and tribromide ion, related to each other by an equilibrium (eq 1), can competitively react with a given compound.[26] The kinetic terms for the free bromine addition and those related to the tribromide ion addition or bromide-assisted bromine addition can be obtained separately, according to the usual equation[26] (eq 2)

$$Br_2 + Br^- \rightleftarrows Br_3^- \qquad (1)$$

$$k_{exp}(1 + K[Br^-]) = \alpha + \beta[Br^-] \qquad (2)$$

in which K is the bromine−tribromide equilibrium constant (eq 1), α is the rate coefficient k_{Br_2} for the bromine addition, and β is the salt effect coefficient. From this coefficient, the rate coefficients "$k_{Br_3^-}$" are readily obtained since, with the hypothesis that the bromide ion effect arises mainly from the competition between free bromine and tribromide ion additions, $\beta = Kk_{Br_3^-}$. In Tables 1 and 2, Q is the $k_{Br_2}/k_{Br_3^-}$ ratio, which expresses the alkene selectivity for the two brominating species. Nevertheless, there has been a controversy[27] about the mechanism to which the β coefficient is to be related. It is now well-established[27,28] that Q values smaller than 15 correspond better to bromide-assisted bromine addition, kinetically equivalent to the tribromide addition. The Q values obtained for the reactions of alkenes **1**−**6**, **9**, and **12** are significantly greater than 15 (except for that of **12** with $Q = 9$) and are in the same range as those observed for the methyl-substituted ethylenes. Therefore, at least for alkenes **1**−**5**, the bromide-assisted bromine addition does not contribute significantly to the experimental bromination rates. The reason why Q for **12** is very small is unclear since small Q values are generally obtained for poorly reactive double bonds for which the assisted

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Table 3. KSIEs in the Bromination of Several Cyclopropyl-Group-Containing Alkenes, Measured at 25 °C

	k_{MeOH}/k_{MeOD}[a]	k_{MeOH}/k_{EtOH}[b]	m[c]
2	1.18 ± 0.07		
3	1.37 ± 0.09		
5		1.90 ± 0.05	(0.30)[d]
6		2.14 ± 0.15	(0.34)[d]
9		1.90 ± 1.2	(0.30)[d]
14[e]	1.35	30.6	0.96
15[e]		20.4	0.92
19[e]		32.0	0.96

[a] KSIE. [b] k_{EtOH} measured in 97.5% aqueous ethanol. [c] Coefficients of the Grunwald−Winstein equation for solvent kinetic effects using Y_{Br^-} solvent parameters, from ref 30. [d] Estimated from k_{MeOH}/k_{EtOH} ratios. [e] From ref 21.

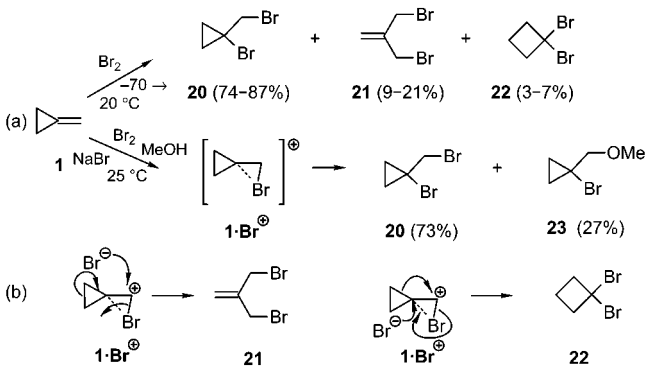
mechanism is favored, yet **12** is highly reactive. The high *Q* value for **6** can be interpreted in terms of a marked steric effect on the $k_{Br_3^-}$ pathway and/or a very high rate for the free bromine addition since it is known[29] that both effects increase the *Q* values strongly.

Some kinetic solvent isotope effects (Table 3) have also been measured with respect to estimating the magnitude of charge development in the rate-limiting transition states of the bromine addition to these cyclopropyl-group-containing alkenes. In the lowest reactivity range, the kinetic solvent isotope effects (KSIEs), k_{MeOH}/k_{MeOD}, have been determined for the reactions of alkenes **2** and **3** by measuring the rate coefficients in MeOD, $k_{MeOD}(\mathbf{2}) = (4.3 \pm 0.3) \times 10^3$ mol^{-1} L s^{-1} and $k_{MeOD}(\mathbf{3}) = (4.0 \pm 0.2) \times 10^4$ mol^{-1} L s^{-1}, respectively (Table 3). Whereas for **3** this KSIE is in the usual range for alkene brominations,[31] that for **2** is noticeably smaller. In the higher reactivity range, the effect of changing the solvent from methanol to 97.5% aqueous ethanol on the reactivity of **5**, **6**, and **9** [$k_{EtOH} = (8.58 \pm 0.03) \times 10^5$, $(1.63 \pm 0.08) \times 10^7$, and $(1.6 \pm 0.2) \times 10^8$ mol^{-1} L s^{-1}, respectively] is surprisingly small as compared to that generally observed for acyclic alkenes.[21] These results, analogous to those previously obtained in the solvolysis of analogous substrates,[32] will be discussed below (vide infra).

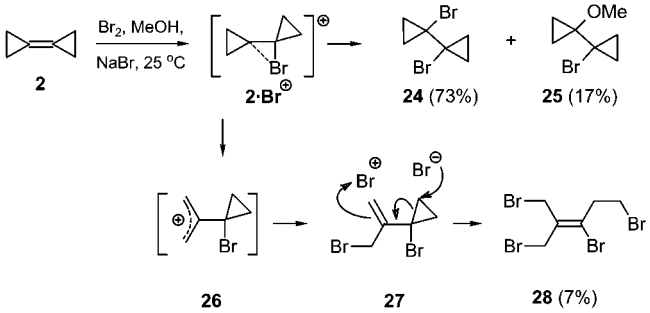
Product Distribution in the Bromination of Hydrocarbons 1−6 in Methanol. Previously, the bromination of **1** in aprotic solvents (pentane, Et_2O, CCl_4)[5a−f] has been reported to yield, in addition to the regular bromine adduct **20**, the two isomeric dibromides **21** and **22** in varying proportions depending on the solvent and the temperature (Scheme 1a, the yields from GC analyses of the reaction mixtures).

In contrast to this, the bromination of **1** in methanol in the presence of 0.42 M sodium bromide yielded only two products, **20** and **23**, in a ratio of 2.7:1. The fact that no product with the isobutene skeleton of type **21** was formed indicates that in methanol only the (1-bromocyclopropyl)methyl cation **1·Br**$^+$ is additionally stabilized by solvation and therefore has no tendency to stabilize

Scheme 1



Scheme 2



itself by rearrangement.[33] Nucleophilic assistance of the polar solvent methanol[34] apparently prevents the ring opening and ring enlargement of **1·Br**$^+$ to yield isobutene derivatives of type **21** or cyclobutane derivatives of type **22**[6c] via nucleophilic attack of bromide anion (Scheme 1b). In the case of **2**, the formation of a cyclopropyl cation fragment as in **2·Br**$^+$ is inevitable (Scheme 2). Therefore, side by side with the direct trapping products **24** (73%) and **25** (17%), the tetrabromo-substituted 2-methyl-2-pentene derivative **28** (7%) was also formed. The tetrasubstituted alkene **28** must arise via ring opening of the cyclopropyl cation moiety in **2·Br**$^+$ to an allyl cation, **26**,[33] and subsequent bromine addition to the allyl bromide **27** with concurrent cyclopropylcarbinyl to homoallyl cation rearrangement. Two additional minor products (about 1.5% each) could not be identified. Upon bromination of **2** in pentane at −30 °C, 1,1′-bis(1-bromocyclopropyl) (**24**) was isolated as the sole product in 83% yield.[3]

In contrast to the brominations of **1** and **2**, that of methylenespiropentane (**3**) yielded predominantly the two ring-opening products **31** (20%) and **32** (32%), both resulting from a cyclopropylcarbinyl to homoallyl cation ring opening in the first intermediate **3·Br**$^+$ and subsequent bromine addition to the intermediate (bromovinyl)-cyclopropane **30** (Scheme 3). The formation of **30** from **3·Br**$^+$ can also be rationalized by an S_N2'-type attack of

(29) (a) Ruasse, M.-F.; Argile, A. *J. Org. Chem.* **1983**, *48*, 202−208. (b) Ruasse, M.-F.; Dubois, J.-E. *J. Am. Chem. Soc.* **1984**, *106*, 3230−3234.

(30) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741−5747.

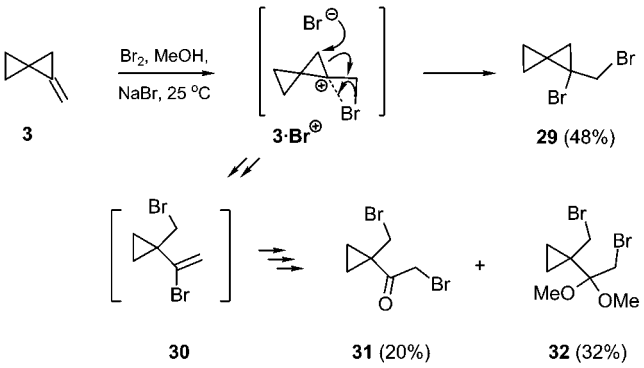
(31) Ruasse, M.-F.; Motallebi, S.; Galland, B. *J. Am. Chem. Soc.* **1991**, *113*, 3440−3446.

(32) (a) Creary, X. *J. Am. Chem. Soc.* **1976**, *98*, 6608−6613. (b) Landgrebe, J. A.; Applequist, D. E. *J. Am. Chem. Soc.* **1964**, *86*, 1536−1542. (c) Späth, T. Dissertation, Universität Göttingen, Göttingen, Germany, 1995. (d) Späth, T.; Kozhushkov, S. I.; Albrecht, K.; Apeloig, Y.; de Meijere, A. To be published.

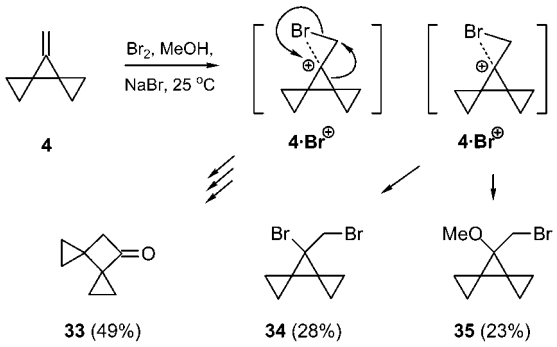
(33) (a) Boche, G.; Walborsky, H. M. In *Cyclopropane Derived Reactive Intermediates*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1990; pp 117−173 and references therein. (b) Friedrich, E. C. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 1987; pp 633−700. (c) Schöllkopf, U. *Angew. Chem.* **1968**, *80*, 603−613; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 588−598. (d) High-level ab initio and DFT calculations show that cyclopropyl cation is not a stationary point on the $C_3H_5^+$ PES, and consequently there is no barrier to ring opening. The allyl cation is 32−36 kcal mol^{-1} more stable. Arnold, P. A.; Carpenter, B. K. *Chem. Phys. Lett.* **2000**, *328*, 90−96.

(34) (a) Stølevik, R.; Bakken, P. *J. Mol. Struct.* **1989**, *197*, 137−142. (b) Buchholz, H. Dissertation, Universität Hamburg, Hamburg, Germany, 1992.

Scheme 3



Scheme 4



bromide on **3·Br**$^+$ with simultaneous ring opening. The actually isolated products **31** and **32** must arise from the methanol trapping of the cationic intermediate in the bromine addition to **30**. Subsequent S_N1 displacement of the bromine α to the methoxy group then yields the dimethyl acetal **32**; fragmentation of the α-bromoether or its hydrolysis gives the α-bromoketone **31**. The rearrangement of **3·Br**$^+$ competitive with its bromine trapping is apparently favored by the additional strain release from its spiropentyl unit in analogy to results from the solvolysis of methylspiropentane derivatives.[3]

The bromination of 7-methylenedispiro[2.0.2.1]heptane (**4**) also gave an important fraction of a rearrangement product, in this case the cyclobutanone **33** (49%) along with the addition products **34** (28%) and **35** (23%) (Scheme 4). In this system, strain release is more favorably accomplished by ring enlargement of the intermediate bromocyclopropylmethyl to a bromocyclobutyl cation, which is trapped by bromide ion or methanol. The isolated cyclobutanone **33** is obviously the hydrolysis product of an initially formed *gem*-dibromide, α-bromoether, or dimethyl acetal (cf.[3b]).

Bromination of the monospirocyclopropanated bicyclopropylidene **5** in methanol gave the three main products **36**, **37**, and **39** in 32%, 48%, and 15% isolated yield, respectively, along with 4% an unidentified compound. According to a gas chromatogram of the crude reaction mixture, the proportions of **36**, **37**, and **39** were 30:50.5:15.5 (Scheme 5). Apparently, all three products are derived from the (1′-bromospiropentyl)-substituted spiropentyl cation **5·Br**$^+$, which must be the thermodynamically favored and more long-lived intermediate. The two major products **36** and **37** (together 80%) were obviously formed directly via **5·Br**$^+$. The remaining product **39** must be derived from the—probably nucleophile-assisted—cyclopropyl to homoallyl ring-opening rearrangement of **5·Br**$^+$ to an intermediate bromomethylenecyclopropane, **38**, which upon further bromination/solvolysis eventually gives the acetal **39**.

Scheme 5

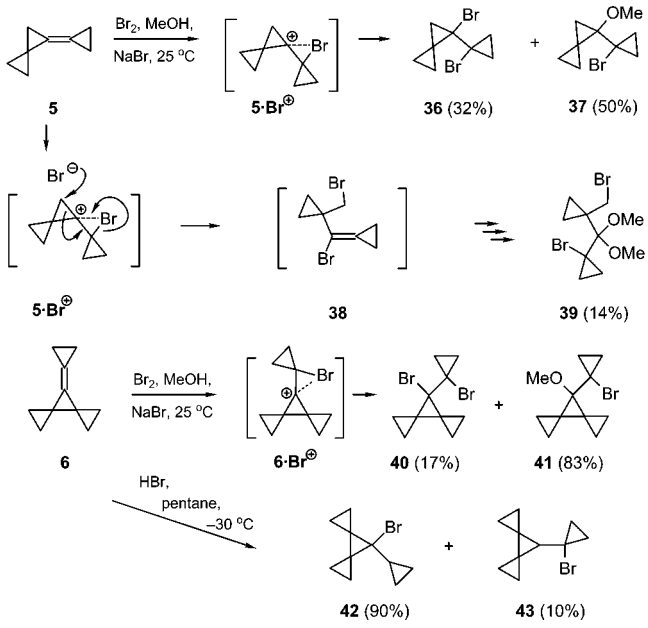


Table 4. Product Distributions in the Bromination of Methylenecyclopropane Derivatives 1−6 in Methanol in the Presence of 0.42 M Sodium Bromide

	nonrearranged adducts[a]			rearranged adducts[b]		
alkene	DB	MB_α	MB_β	A	B	C
1	73	27				
2[c]	73	17	7			
3	48				52	
4	28		23			49
5[c]	32		48		14	
6	17		83			

[a] DB = dibromide, MB_α = anti-Markovnikov-type methoxybromide, derived from (bromocyclopropyl)carbinyl cation intermediates, and MB_β = Markovnikov-type methoxybromide, formally derived from (bromomethyl)cyclopropyl cation intermediates. [b] A = product formally derived from the cyclopropyl to allyl cation rearrangement of the (bromomethyl)cyclopropyl cation, B = product derived from the cyclopropylcarbinyl to homoallyl rearrangement, and C = product formally derived from ring enlargement of the (bromocyclopropyl)carbinyl cation. [c] Plus 3−5% unidentified products.

Finally, 7-cyclopropylidenedispiro[2.0.2.1]heptane (**6**) upon bromination in methanol gave only the two products **40** and **41**, both derived from an intermediate bromocyclopropyl cation, **6·Br**$^+$, which must be very efficiently stabilized by the two adjacent spirocyclopropane groups and one α-cyclopropyl substituent. However, the fact that **6** upon hydrobromination, in addition to **42** (90%), also gives the bromide **43** in 10% yield indicates that the alternative dispiroheptyl-substituted cyclopropyl cation intermediate can also be formed.

Considering the product distributions (Table 4) for the bromine additions to methylenecyclopropane derivatives **1**−**6** in methanol, one can identify three trends.

(1) With an increasing number of spiroannelated three-membered rings on **1**, the total amount of products with retained cyclopropane rings decreases, while increasing spiroannelation on **2** leads to an increasing total amount of nonrearranged products. Corresponding results have been reported for the bromination in pentane, which for compounds **4** and **6** proceeds without ring opening, i.e.,

contrary to hydrocarbons **1** and **2** (see above).[3,18] Hydrobromination of **1** also occurs with ring opening[5b] and that of **4** and **6** without ring opening.[3,18] In the case of **6**, the regioselectivity of 9:1 in favor of the "Markovnikov"-type product **42** is remarkable (Scheme 5).

(2) On going from **1** to **3** and **4**, the predominating reactive intermediate changes from the cyclopropylcarbinyl to the cyclopropyl-type cation. The intermediates formed from **2**, **5**, and **6** inevitably are cyclopropyl-type cations, but spiroannelation of cyclopropane rings apparently stabilizes such cations kinetically and thus leads to a regioselective methoxybromination of **5** and **6** to give **37** and **41**, respectively.

(3) The ratio of products with and without a methoxy group (**24**:**25** ≈ 4:1, **34**:**35** ≈ 1:1, **36**:**37** ≈ 1:1.6, **40**:**41** ≈ 1:5) demonstrates that the lifetime of the cationic intermediates increases with an increasing number of cyclopropane rings directly attached to the double bond or spiroannelated at the cyclopropane ring of the core unit (the longer the lifetime, the more important the methanol trapping of free intermediates and the less important the formation of dibromide by internal ion pair collapse). Steric effects may also contribute to controlling this product ratio as the larger bromide ion may less easily get close to this cation than the smaller methanol molecule. According to MM2 calculations, 1,1′-dibromobicyclopropyl (**24**),[34a] for example, should exist as a *gauche* conformer only, whereas unsubstituted bicyclopropyl exists as an equilibrium mixture of *gauche* and *s-trans* conformers.[35] The rotational barrier for the dibromide **40** was calculated by the MM2 method to be 14.1 kcal/mol,[34b] although a freezing of the conformational changes could not be detected for **40** down to −90 °C.

Computational Studies

Calculations using density functional theory (DFT)[36] on the structures and energies of the methylenecyclopropanes **1**−**6**, the cyclopropyl-substituted alkenes **7**−**12**, the simple acyclic alkenes **13**−**19**, and their bromonium ions **1·Br**$^+$−**19·Br**$^+$ were carried out.[37] The geometries of all the molecules were optimized using the hybrid density functional method at the B3LYP//6-311G(d,p) level of theory.[38,39] 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 a transition state (one imaginary frequency).

Structures of Bromonium Ions. The structures of bromonium ions **1·Br**$^+$−**19·Br**$^+$ were calculated, and the geometries of most of them are shown in Figure 1.[40] The intermediate in the bromination of ethylene is a C_{2v}-symmetric bromonium ion, **13·Br**$^+$, with relatively long C−Br bonds of 2.053 Å (compared to 1.929 Å in CH_3Br), thus enclosing a very acute C−Br−C bond angle of 41.4°. This structure is in good agreement with previous ab initio calculations at the MCSCF level (effective core potentials with an uncontracted basis set composition of 5s5p were used), which reports C−Br bond lengths of 2.069 Å and a C−Br−C bond angle of 41.2°.[12i] Hamilton and Schaefer carried out both SCF and CISD calculations using a DZ+d basis set, and their calculated C−Br bond lengths were 2.053 and 2.025 Å, respectively.[12j] The good agreement between these high-level ab initio calculations[12i,j] and the current DFT calculations supports the reliability of the B3LYP/6-311G(d,p) calculations for describing these species. The intermediate from tetramethylethylene, the bromonium ion **19·Br**$^+$, has significantly longer C−Br bonds of 2.176 Å, and a correspondingly smaller C−Br−C bond angle of 39.8°.

The calculated geometry of **19·Br**$^+$ may be compared with crystallographic data on the bromonium ion of adamantylideneadamantane, which revealed an average C−Br bond length of 2.11 Å and an average C−Br−C bond angle of 41.3°,[12i] in reasonable agreement with the calculations for **19·Br**$^+$.

The bromonium ion **15·Br**$^+$ resulting from isobutene is highly unsymmetrical with a relatively short C−Br bond of 2.001 Å (1.929 Å in CH_3Br) to the primary carbon (solid line in the structure of **15·Br**$^+$ in Figure 1) and a significantly longer C−Br bond of 2.382 Å to the tertiary carbon (dashed line in the structure of **15·Br**$^+$ in Figure 1). This is the expected structure **15·Br**$^+$, as it places a higher positive charge (+0.57, Figure 2) on the tertiary CMe_2 group than on the primary CH_2 group (+0.12). The central C−C bond distances in **13·Br**$^+$, **15·Br**$^+$, and **19·Br**$^+$ of 1.451, 1.464, and 1.482 Å, respectively, are significantly longer than that of a C=C double bond (1.333 Å in $Me_2C{=}CH_2$), indicating that these species are better described as bromonium ions rather than as π-complexes.[41]

The spirocyclic bromonium ion **1·Br**$^+$ from methylenecyclopropane is much more symmetrical than **15·Br**$^+$, the C−Br distances being 2.034 Å to the primary carbon and 2.149 Å to the tertiary carbon, and the calculated positive charge on the primary CH_2 group (+0.23) is somewhat smaller than on the cyclopropyl group (+0.34, see Figure 2). The C−C bond length (1.440 Å) is slightly shorter than in **15·Br**$^+$, but again much longer than in the corresponding alkene **1** (1.318 Å). The spiroannelation of a cyclopropane ring as in **3** has a strong effect on the structure of the corresponding bromonium ion **3·Br**$^+$, which is highly unsymmetrical with a short C−Br bond of 1.993 Å to the primary carbon and a very long C−Br bond of 2.521 Å to the tertiary carbon; the C−C−Br bond angle is 92.9°. This structure is in line with the fact that

(35) Bastiansen, O.; de Meijere, A. *Acta Chem. Scand.* **1966**, *20*, 516−521; Hagen, K.; Hagen, G.; Traetteberg, M. *Acta Chem. Scand.* **1972**, *26*, 3649−3661.

(36) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, Germany, 2000.

(37) The Gaussian series of programs was used. GAUSSIAN 98, revision A.7: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1998.

(38) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785−789.

(39) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639−5648. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650−654.

(40) No attempt was made to locate the weakly bound π-complexes between the alkenes and Br_2.

(41) Olah, G. A. *Carbocations and Electrophilic Reactions*; Wiley: New York, 1973; pp 113−116.

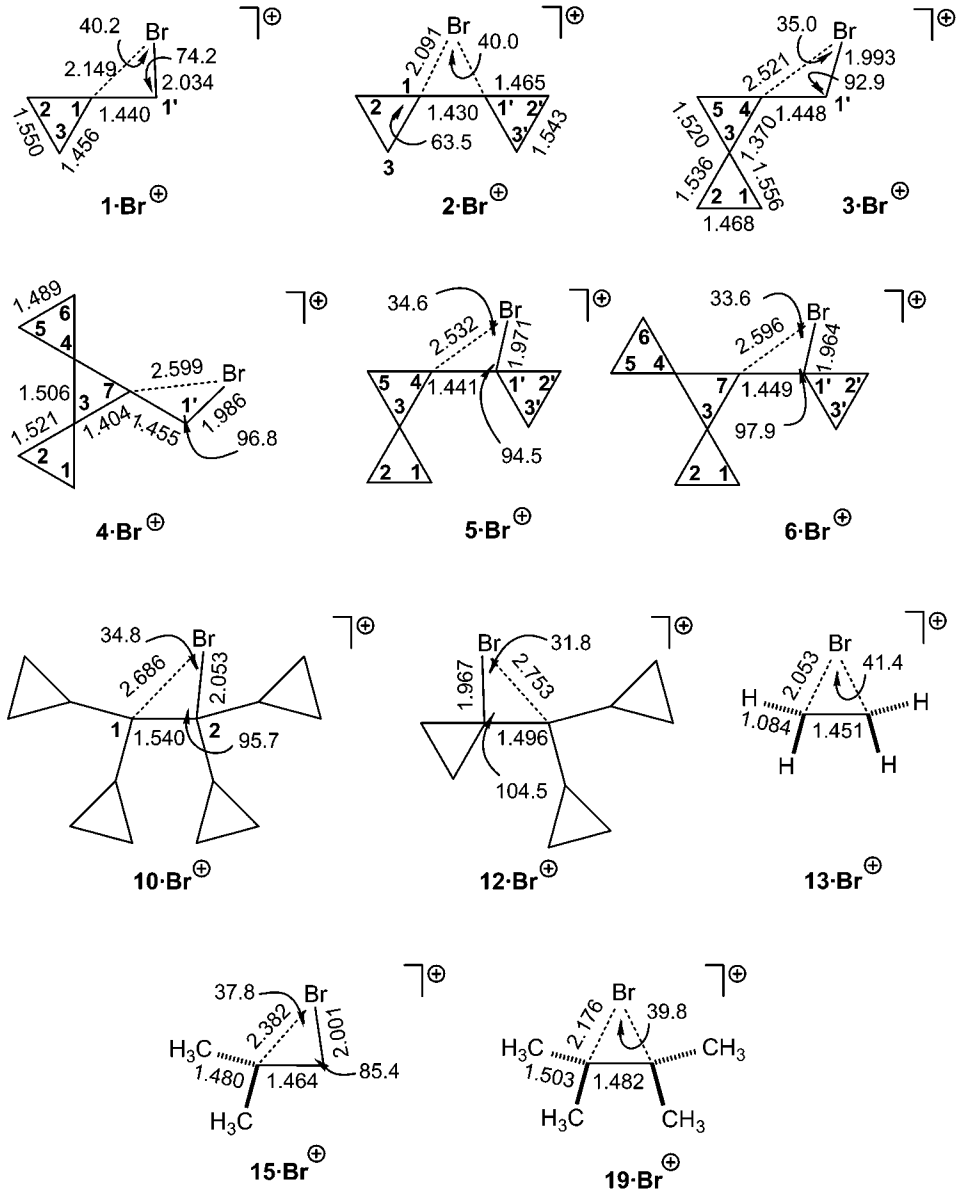


Figure 1. Calculated [B3LYP/6-311G(d,p)] geometries (bond lengths in angstroms, bond angles in degrees) of bromonium cations.

a cyclopropyl substituent strongly stabilizes an adjacent positively charged center[42] and thus favors an unsymmetrical structure that places a larger positive charge at the cyclopropyl carbon, as shown in structure **3·Br**$^+$ (Figure 2). In analogy to **3·Br**$^+$, the bromonium ion **4·Br**$^+$, which has two spiroannelated cyclopropane rings, is also highly unsymmetrical (the C−Br bond lengths are 1.986 Å for C$^{1'}$−Br and 2.599 Å for C^7−Br), the positive charge at the cyclopropyl carbon being strongly stabilized by the two adjacent spirocyclopropane rings.

The bromonium ion **2·Br**$^+$ from bicyclopropylidene is again symmetrical with C−Br bond distances of 2.091 Å, shorter by 0.085 Å than in the tetramethylethylene analogue **19·Br**$^+$. The bromonium ions of the spirocyclopropanated bicyclopropylidenes, **5·Br**$^+$ and **6·Br**$^+$, are highly unsymmetrical with one short and one long C−Br bond (Figure 1) in analogy to **3·Br**$^+$ and **4·Br**$^+$. The bromonium ion **10·Br**$^+$ from tetracyclopropylethylene also is not symmetrical, and this results from the different orientations of the cyclopropyl rings relative to the CBrC ring, which reduce the symmetry of the bromonium ion.[43]

Bromination Rates. Theory vs Experiment. To quantify the nucleophilicity of the double bond in the various alkenes **1**−**12**, the energy changes (ΔE) for the addition of Br$^+$ to these alkenes were calculated (see Table 5).[44] For comparison, ΔE values were also computed for the analogous methyl-substituted ethylenes **13**−**19**.

In the gas phase, the addition of Br$^+$ to all alkenes is, as expected, highly exothermic, e.g., by −103.0 kcal mol^{-1}

(42) Smith, M. B.; March, J. *March's Advanced Organic Chemistry. Reactions, Mechanisms, and Structure,* 5th ed.; Wiley: New York, 2001; Chapter 5, pp 222−223.

(43) The highly unsymmetrical structure of **10·Br**$^+$ results from the fact that the cyclopropyl rings attached to C^1 rotate into a bisected conformation, which strongly stabilizes the positive charge at this site. For steric reasons the four cyclopropyl groups cannot simultaneously adopt the preferred bisected conformation.

(44) Initially, an attempt was made to quantify the nucleophilicity of the double bond by calculating the proton affinities of these alkenes. However, no correlation was found between the bromination rates and the proton affinities.

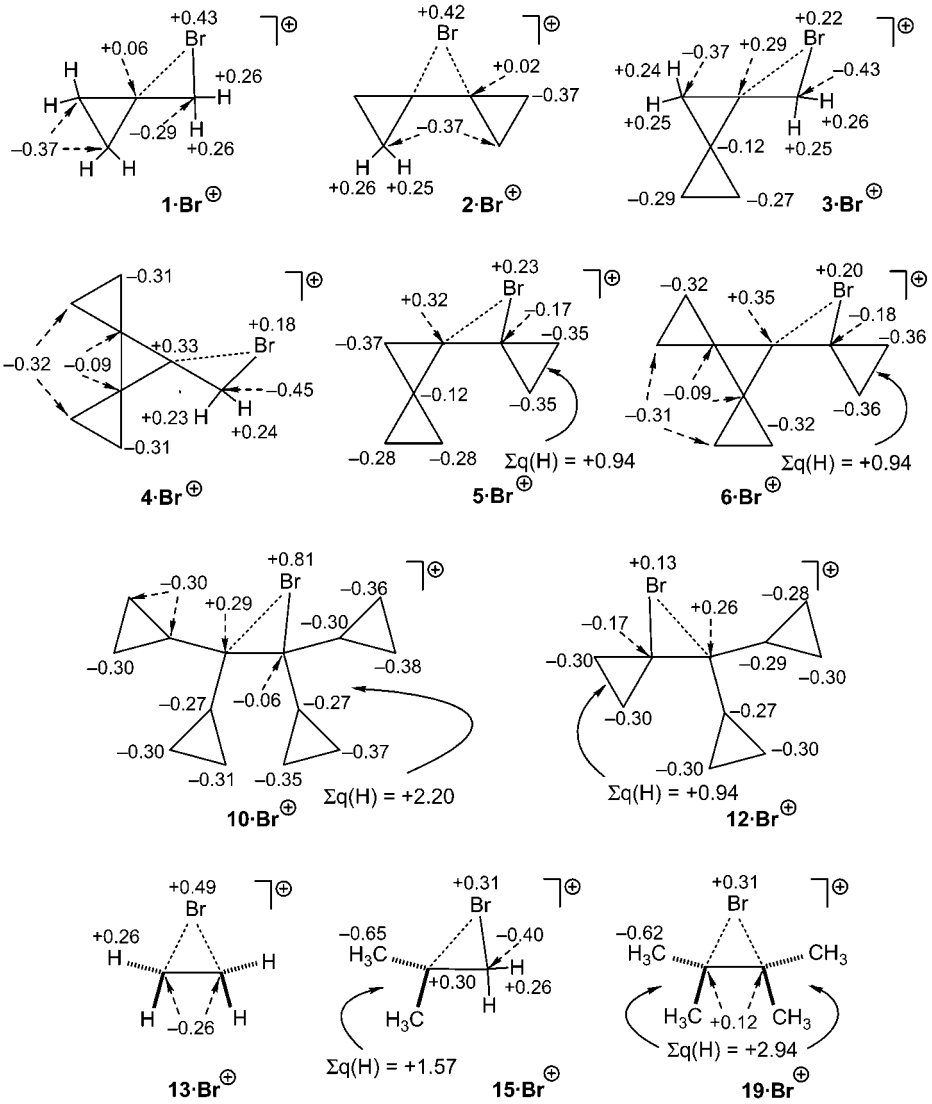


Figure 2. Calculated [B3LYP/6-311G(d,p)] NPA charges of bromonium cations. [∑q(H) denotes the sum of the charges on the hydrogens in the fragments which are pointed at by the arrows (e.g., in **5·Br**$^+$ it refers to one cyclopropyl ring and in **10·Br**$^+$ to two rings).

Table 5. Calculated Energies [B3LYP/6-311G(d,p) + ZPE, kcal mol^{-1}] for the Addition of Br$^+$ to Various Alkenes 1−19 and the Corresponding Experimental Bromination Rate Constants (k_{Br_2}) for the Addition of Bromine to Alkenes 1−19 in Methanol at 25 °C

alkene	ΔE^a	$\Delta\Delta E^b$	log k_{Br2}	alkene	ΔE^a	$\Delta\Delta E^c$	log k_{Br2}
1	−114.2	−0.0	2.56	**13**	−103.0	0.0	0.67
2	−123.8	−9.7	4.67	**14**	−112.2	−9.2	2.61
3	−123.7	−9.6	3.77	**15**	−120.5	−17.5	4.57
4	−130.5	−16.4	5.29	**16**	−119.6	−16.7	4.38
5	−132.1	−17.9	6.21	**17**	−119.4	−16.4	
6	−138.7	−24.5	7.53	**18**	−126.1	−23.2	6.11
7	−126.9	−12.8		**19**	−131.0	−28.0	7.09
8	−143.1	−28.9		**7**	−126.9	−24.0	
9	−142.2	−28.0	8.48	**8**	−143.1	−40.1	
10	−140.9	−26.7		**9**	−142.2	−39.2	8.48
11	−141.2	−27.0		**10**	−140.9	−37.9	
12	−153.7	−39.5	8.90				

[a] Energy changes for the addition of Br$^+$ to the alkene. [b] Arithmetic difference in the calculated ΔE relative to that of **1**. [c] Arithmetic difference in the calculated ΔE relative to that of **13**.

for ethylene. For calibration against solution results, it is useful to compare the calculated ΔE values for the alkenes of interest relative to that of a reference system. This is conveniently done by the use of isodesmic Br$^+$ exchange equations, such as eq 3, in which **Alk** denotes

$$\mathbf{15{\cdot}Br^+ + Alk \rightarrow 15 + Alk{\cdot}Br^+} \qquad (3)$$

an alkene (e.g., **1**−**6**) and **Alk·Br**$^+$ denotes its bromonium ion. Equation 3, for example, compares the Br$^+$ addition energies of several alkenes (**Alk**) relative to that of **15**, and the calculated energy values are given in Table 6. Similarly, the $\Delta\Delta E$ values in Table 5 give the energies of similar Br$^+$ transfer reactions relative to that of **1** (left half of Table 5) or relative to that of ethylene (**13**) (right half of Table 5).

Table 6. Calculated Energies [B3LYP/6-311G(d,p) + ZPE] of Br$^+$ Exchange According to Eq 3 for Alkenes 1−6

Alk	**1**	**2**	**3**	**4**	**5**	**6**
ΔE (kcal mol^{-1})	6.3	−3.3	−3.2	−10.0	−11.6	−18.2

The ΔE values for the addition of Br$^+$ to the methyl-substituted ethylenes **13**−**19** show a straightforward correlation with the number of methyl groups connected to the double bond. The $\Delta\Delta E$ value [i.e., the stability (in this paper the term stability refers to thermodynamic stability) of a particular bromonium ion relative to that of the parent **13·Br**$^+$] for propene is by 9.2 kcal mol^{-1}

lower than for ethylene, and that for isobutene is lower yet by another 8.3 kcal mol^{-1} (i.e., **15·Br**$^+$ is more stable by 17.5 kcal mol^{-1} than **13·Br**$^+$). Substitution of ethylene with a third and a fourth methyl group stabilizes the bromonium ion further by ca. 6 and 5 kcal mol^{-1}, respectively. The mean stabilizing effect of each methyl substituent on the bromonium ion is thus ca. 7 kcal mol^{-1}.

The bromonium ion **1·Br**$^+$ derived from **1** is less stable by 6.3 kcal mol^{-1} than the bromonium ion **15·Br**$^+$ derived from isobutene (eq 3, **Alk** = **1**).[45] A spiroannelated cyclopropane ring as in **3** and **4** stabilizes the bromonium ion versus **1·Br**$^+$ by 9.6 kcal mol^{-1} for the first ring (i.e., **3·Br**$^+$) and by an additional 6.8 kcal mol^{-1} for the second ring (Table 5), so that **4·Br**$^+$ is 10 kcal mol^{-1} more stable than **15·Br**$^+$ (eq 3, **Alk** = **4**). The stabilizing effect by a spirocyclopropane ring is similar on going from the bromonium ion of bicyclopropylidene, **2·Br**$^+$, to that of cyclopropylidenespiropentane, **5·Br**$^+$, and cyclopropylidenedispiro[2.0.2.1]heptane, **6·Br**$^+$, for which the stabilizing effect is 8.2 kcal mol^{-1} for the first ring and an additional 6.6 kcal mol^{-1} for the second ring (Table 5). Thus, spiroannelation of a cyclopropane ring in the α-position to the double bond of a methylenecyclopropane or bicyclopropylidene stabilizes the bromonium ion on the average by 8−9 kcal mol^{-1} for the first ring, and by yet another ca. 7 kcal mol^{-1} for the second ring (Table 5). Direct substitution of ethylene by cyclopropyl groups as in **7**−**10** or on the methylene group of methylenecyclopropane as in **11** and **12** leads to a much larger stabilization of the bromonium ion, e.g., by as much as 27.0 kcal mol^{-1} for one α-cyclopropyl group in **11·Br**$^+$ and by 39.5 kcal mol^{-1} for two groups in **12·Br**$^+$ relative to **1·Br**$^+$.

The calculated energies (according to eq 3 or the $\Delta\Delta E$ values in Table 5) correlate with the relative rates of bromination of the corresponding alkene[46] (correlation coefficient 0.927 according to eq 4, Figure 3). The quality of the correlation is particularly impressive considering the wide variety of alkenes included, and the fact that the calculations are related directly only to the gas phase, neglecting solvation effects. The correlation coefficient improves significantly when only structurally related alkenes are included as done in Figure 4. Thus, when only the methyl-substituted ethylenes are considered, according to eq 5, the correlation coefficient is as high as 0.998 (Figure 4a). Similarly, for the bicyclopropylidenes **2**, **5**, and **6**, the correlation coefficient is 0.999, and for the methylenecyclopropanes **1**, **3**, and **4**, it is 0.974 (Figure 4b).

$$\log k_{Br_2} = -0.171\Delta\Delta E + 2.956 \qquad (4)$$

$$\log k_{Br_2} = -0.233\Delta\Delta E + 0.570 \qquad (5)$$

A calculated $\Delta\Delta E$ of 1.36 kcal mol^{-1} between two transition states is reflected in a rate enhancement by a factor of 10 at 25 °C. Comparison of the calculated $\Delta\Delta E$ values and the experimental bromination rates in methanol shows that the actual rate changes observed in solution are much smaller than the calculated ones. For example, **15** is brominated 102 times faster than **1**, while the calculated $\Delta\Delta E$ for these two alkenes (eq 3, **Alk** = **1**) is 6.3 kcal mol^{-1} corresponding to a predicted rate enhancement of $10^{4.5}$. Similarly, **3** and **4** are predicted by their calculated $\Delta\Delta E$ values to react 10^7 and 10^{12}, respectively, faster than **1**, while actually they are brominated only 16 and 537 times, respectively, faster than **1** (Table 5). These large differences between the $\Delta\Delta E$ values calculated for the gas phase and the actual rate enhancements observed are due to at least two major factors: (a) solvation effects, which in solution significantly reduce the magnitude of the substituent effects on the bromination rates relative to that in the gas phase, and (b) the fact that only part of the electronic and steric effects, operating in the bromonium ions, are experienced also in the transition states. The slope of the correlation line in Figure 3 of −0.171 gives a qualitative measure of these effects. Namely, the effect of the substituents is reduced in the experiments by a factor of 5.5 in terms of energy and by a factor of ca. $10^{5.5}$ in terms of rates relative to that of the fully developed respective bromonium ions in the gas phase. The relatively small slope suggests a relatively "early" transition state with only little "bromonium ion character" and/or a leveling of the substituent effects by the solvent. This is in line with previous conclusions of various experimental studies (see below).

The good correlation according to eq 4 means that substituents which strongly stabilize a bromonium ion will also significantly enhance the bromination rate for the corresponding alkene. For instance, **12·Br**$^+$ is more stable than **1·Br**$^+$ by 39.5 kcal mol^{-1}, and correspondingly **12** is brominated 2×10^6 times faster than **1** (Table 5). Both the calculations and the experiments point to a much larger effect of an α-cyclopropyl substituent than that of a spirocyclopropane group or a methyl substituent.

The influence of cyclopropyl substituents on the double bond of ethylene is somewhat different from that on the double bond of methylenecyclopropanes **11** and **12**. For ethylene, successive α-substitution with up to two cyclopropyl groups enhances the rate drastically whereas a third and a fourth cyclopropyl substituent retards the rate slightly. This kinetic series is also nicely reproduced by the calculations of the corresponding bromonium ions. The first α-cyclopropyl substituent on ethylene leads to a stabilization of the bromonium ion by 23.9 kcal mol^{-1} (Table 5), and the second stabilizes the bromonium ion further by 16.2 kcal mol^{-1} (total effect of 40.1 kcal mol^{-1}). The effect is similar in the methylenecyclopropanes **11** and **12**, where the stabilization by the first and second cyclopropyl groups is 27.0 and 39.5 kcal mol^{-1}, respectively (Table 5). In contrast, substitution on ethylene by a third and a fourth α-cyclopropyl group on ethylene *destabilizes* the bromonium ion by 0.9 and 1.3 kcal mol^{-1}, respectively. This rate retardation can be reasonably attributed to rate-decreasing steric and *σ*-electron-withdrawing effects of the additional cyclopropyl groups with inappropriate orientations which override the rate-increasing electron-donating effects of the cyclopropyl groups.

A fairly good linear relationship (Figure 5, $r^2 = 0.934$) is also found between the bromination rate coefficients of the alkenes and their first ionization energies as taken from their PE spectra.[22] An analogous relationship[47] has previously been observed for acyclic alkenes with linear *n*-alkyl substituents and attributed to the absence of any steric control in the bromination rates.

(45) As the two bromonium ions have the same number of carbon atoms, "size effects" are not important. Similarly, **2·Br**$^+$ is less stable than **19·Br**$^+$ by 7.2 kcal mol^{-1}.

(46) The same qualitative behavior was obtained also when ΔE and $\Delta\Delta E$ values were replaced by the corresponding ΔG and $\Delta\Delta G$ values although in Figure 2 the correlation coefficient was somewhat lower.

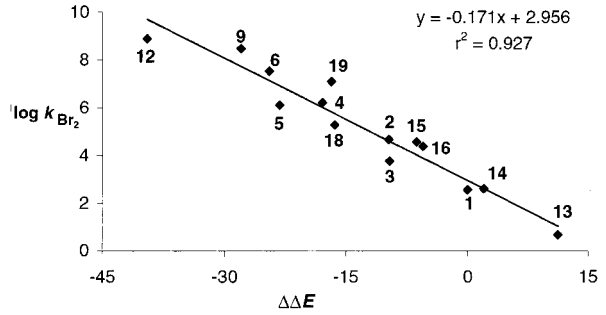


Figure 3. Measured rates of bromination of alkenes **2**−**19** versus their calculated $\Delta\Delta E$ values [B3LYP/6-311G(d,p) + ZPE] relative to the energy of **1**.

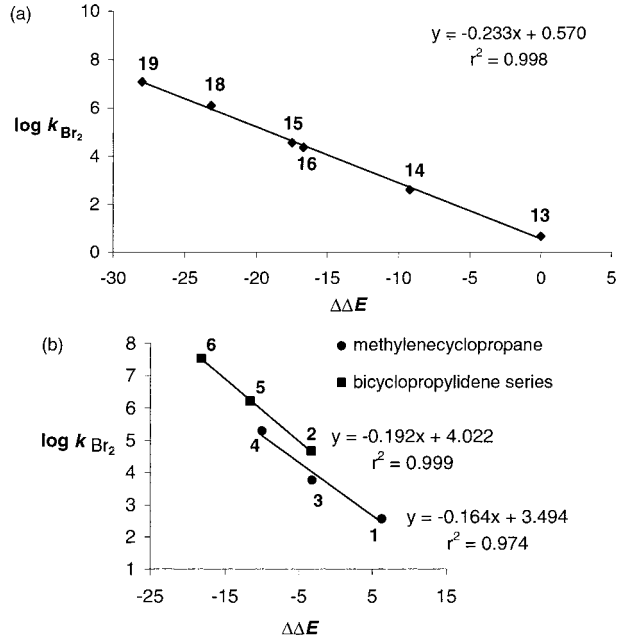


Figure 4. Measured rates of bromination versus calculated $\Delta\Delta E$ values [B3LYP/6-311G(d,p) + ZPE]: (a) methyl-substituted ethylenes **13**−**19** relative to ethylene and (b) methylenecyclopropane series (**1**, **3**, **4**) and bicyclopropylidene series (**2**, **5**, **6**) relative to isobutene.

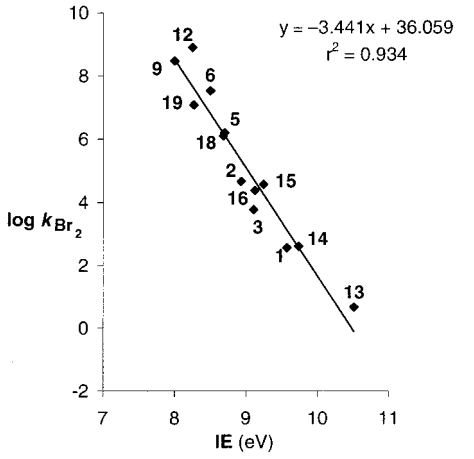
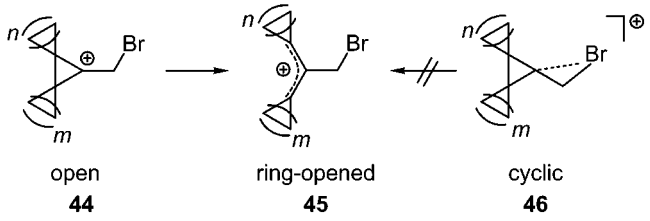


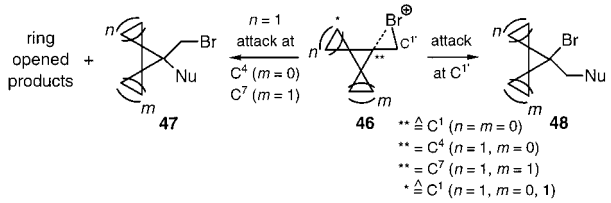
Figure 5. Measured rates of bromination of various alkenes versus their π-IEs.

In the same way as for the rate-calculated energy relationships, better correlations are obtained when methylethylenes **13**−**19** (eq 6 with $r^2 = 0.991$) and

Scheme 6



Scheme 7



cyclopropanated alkenes **1**−**12** (eq 7 with $r^2 = 0.963$) are considered separately.

$$\log k_{Br_2} = -2.936(IE) + 31.424 \quad (6)$$

$$\log k_{Br_2} = -5.007(IE) + 49.879 \quad (7)$$

Bromination Products. Theory vs Experiment. As it is well established that cyclopropyl cations undergo ring opening to the more stable allyl cations,[33] the fact that the major bromination products of most methylenecyclopropanes contain an intact central ring indicates that simple cyclopropyl cations **44** are not intermediates in these reactions, and that their solvation makes their reaction with methanol faster than their rearrangement. Indeed, the calculations show that the reaction intermediates are not simple bromine-substituted cyclopropyl cations **44**, but bridged bromonium ions of type **46** (Scheme 6). Even though some of the calculated bromonium ions are highly unsymmetrical (e.g., **3**·Br^+), there is still a significant interaction between the bromine and the adjacent positively charged cyclopropyl center. **1**·Br^+ is calculated to be 8.6 kcal mol^{-1} less stable than its corresponding allyl cation **45** ($m = n = 0$), but a small barrier of 1.6 kcal mol^{-1} for ring opening slows the rearrangement. In solution the barrier for ring opening is probably higher.

As to the attack of a nucleophile on a bromonium ion, it is reasonable that it will occur at the carbon atom which carries the highest positive charge. The calculated natural population analysis (NPA) charge distributions (given in Figure 2) show that for all unsymmetrical bromonium ions the charge on $C^{4(7)}$ (see atom numbering in Figure 1 and Scheme 7) is positive while it is negative on $C^{1'}$. E.g., for **3**·Br^+, **4**·Br^+, **6**·Br^+, and **15**·Br^+ the charges on $C^{4(7)}$ are +0.29, +0.33, + 0.35, and +0.30, respectively, and the charges on $C^{1'}$ are −0.43, −0.45, −0.18, and −0.40, respectively. Thus, in such ions, where the $C^{1'}$−Br bond is substantially shorter than the $C^{4(7)}$−Br bond, and the positive charge on $C^{4(7)}$ is larger than on $C^{1'}$, attack is expected to occur preferably at the more highly charged $C^{4(7)}$ (Scheme 7). In agreement with these qualitative theoretical considerations, in the bromination

(47) (a) Dubois, J.-E.; Chrétien, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 3506−3513. (b) Chrétien, J. R.; Coudert, J.-D.; Ruasse, M.-F. *J. Org. Chem.* **1993**, *58*, 1917−1921.

of, e.g., **4** and **6** via the highly unsymmetrical ions **4·Br**$^+$, **6·Br**$^+$, products of a nucleophilic attack at $C^{4(7)}$ were observed (i.e., **35** and **41** in Schemes 4 and 5). Furthermore, as the charge at the cyclopropyl $C^{4(7)}$ (and the groups attached to it) increases, the driving force for ring opening increases, and some charge is also transferred to C^1, increasing its reactivity toward nucleophiles. In agreement with these qualitative theoretical considerations, the bromination of **3** (via unsymmetrical **3·Br**$^+$) yields products that result from cyclopropyl ring opening as well as from nucleophilic attack at C^1 (see Scheme 3). It is noteworthy that the calculated structures of the bromonium ions, more specifically their asymmetry, is in complete agreement with the structures used in Schemes 1−5 to rationalize the observed products.

The only case where the nucleophilic attack occurs at $C^{1'}$ is observed in the bromination of **1** (via **1·Br**$^+$), which produces **23** in a yield of 27%, and no product resulting from an attack at C^1 (corresponding to C^4 in **3** and C^7 in **4**, respectively) is observed. This experimental result seems to contradict the calculated charge distribution. However, a hint for this exceptional behavior can already be found in the very small positive charge of +0.06 on C^1 in **1·Br**$^+$. Furthermore, in **1·Br**$^+$ the total positive charge on $C^{1'}H_2$ is considerably larger than found in all other bromonium ions (e.g., +0.23 in **1·Br**$^+$ vs +0.08 in **3·Br**$^+$ or +0.02 in **4·Br**$^+$), while the total positive charge on the fragment that contains $C^{1(4/7)}$ is significantly smaller in **1·Br**$^+$ than that in all other bromonium ions (for example, it is +0.34 in **1·Br**$^+$ vs +0.7 and +0.8 in **3·Br**$^+$ and **4·Br**$^+$, respectively, Figure 2). A theoretical quantitative rationalization for the exceptional behavior of **1·Br**$^+$ is given below.

To account more quantitatively for the various products obtained in the brominations, the transition states for nucleophilic attack at $C^{1'}$, $C^{1(4/7)}$, and C^1 (see Scheme 7), as well as for ring opening, would have to be calculated. As such calculations are very resource demanding, they were conducted only for the parent **13·Br**$^+$, for the dimethyl-substituted **15·Br**$^+$, and for the methylenecyclopropane-derived bromonium ion **1·Br**$^+$, which behaves differently than the other bromonium ions. A water molecule was chosen as an appropriate model for the attacking nucleophile.[48]

According to the calculated profiles for these reactions (Figure 6), the first step involves the exothermic formation of a bromonium ion−water complex, and this is followed by a transition state (TS) that leads to the products. For the parent bromonium ion **13·Br**$^+$, the formation of the complex is exothermic by 21.8 kcal mol^{-1} (relative to the isolated reactants), and the TS that follows involves a barrier of 6 kcal mol^{-1}, leading to a product which is very close in energy to that of the complex (Figure 6a). Water attack on the unsymmetrical **15·Br**$^+$ exhibits a very different potential energy surface (Figure 6b). While water attack at C^1 is exothermic by 21.5 kcal mol^{-1} (relative to the isolated reactants), the attack at $C^{1'}$ is calculated to be endothermic by ca. 1 kcal mol^{-1}.

The same conclusion is valid if the bromonium ion−water complex is taken as the reference point; the reaction leading to products via water attack at $C^{1'}$ is endothermic by 7.4 kcal mol^{-1}, while the attack at C^1 is exothermic by 7.4 kcal mol^{-1}. Furthermore, with **15·Br**$^+$ the TS corresponding to attack at $C^{1'}$ involves a high barrier of 11.1 kcal mol^{-1}, but the TS corresponding to attack at C^1 has a low barrier of 5.0 kcal mol^{-1}. Thus, for **15·Br**$^+$, nucleophilic attack at C^1 is predicted to be strongly preferred over attack at $C^{1'}$, both thermodynamically and kinetically (Figure 6b). As pointed out above, this preference can also be related to the higher positive charge (+0.30) placed on the tertiary C^1 of **15·Br**$^+$. The theoretical finding is in good agreement with the experimental observation that bromination of isobutene in methanol gives the Markovnikov-type product $Me_2C(OMe)CH_2Br$ in 85% yield, and none of the isomer corresponding to nucleophilic attack at $C^{1'}$.[47b]

In the case of **1·Br**$^+$, water addition to either $C^{1'}$ or C^1 is exothermic (Figure 6c). Addition to C^1 leading to **51** (Scheme 8) is exothermic by 27.5 kcal mol^{-1} (relative to

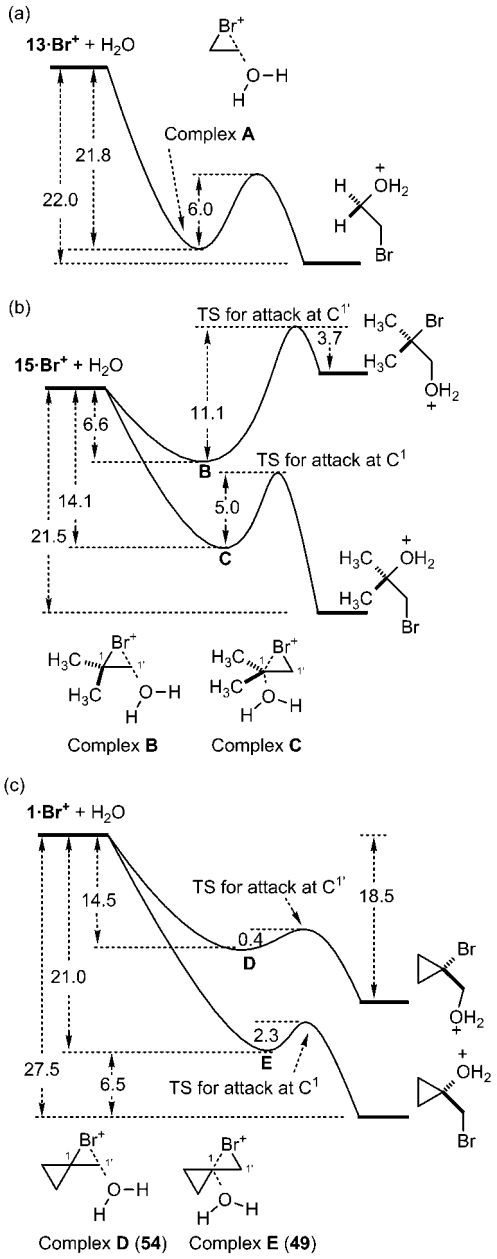
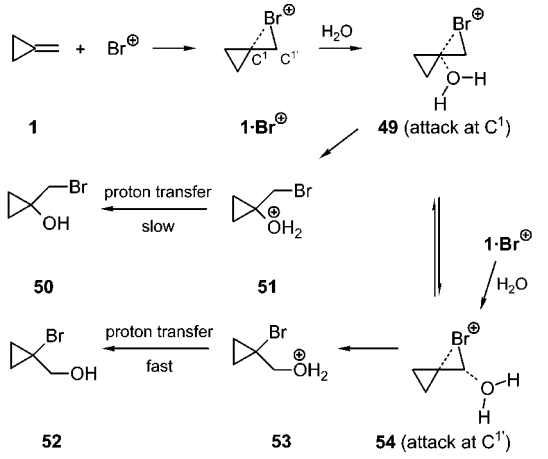


Figure 6. Calculated [B3LYP/6-311G(d,p)] energy profiles (kcal mol^{-1}) for the attack of water at $C^{1'}$ and C^1 of (a) **13·Br**$^+$, (b) **15·Br**$^+$, and (c) **1·Br**$^+$.

(48) We note that this model in which only one water molecule models the solvent is extremely simplified, but we assume that some insight can nevertheless be gained by the calculations detailed below.

Scheme 8



the reactants), while addition to $C^{1'}$ leading to the isomeric **53** is exothermic by only 18.5 kcal mol^{-1} (Figure 6c). Thus, the product resulting from attack at C^1 is favored thermodynamically. The same conclusion is valid also if the bromonium ion−water complex is taken as the reference point; the reactions leading from the complexes **49** and **54** to **51** and **53** are exothermic by 6.5 and 4.0 kcal mol^{-1}, respectively (Figure 6c). However, for **1·Br**$^+$, the transition state leading to **51** is calculated to have an energy barrier of 2.3 kcal mol^{-1}, whereas the transition state leading to **53** has a very low barrier of 0.4 kcal mol^{-1}. This lower barrier for attack at $C^{1'}$ is consistent with the formation of product **23** (in 27% yield) in the bromination of **1** in methanol, and the absence of products of type **50**. Thus, the product formation from **1** is kinetically controlled. This solves the apparent contradiction pointed out above between the calculated charge distributions in **1·Br**$^+$ and the observed products.

Finally, it is of interest to compare in the addition of water to **1·Br**$^+$ the geometries of the bromonium ion−water complexes and the transition states leading to products. Both the complex and the TS appear "later" on the reaction coordinate for attack at C^1 compared to attack at $C^{1'}$. The C---OH_2^+ distance is 2.572 Å in the $C^{1'}$ complex **54** and 1.572 Å in the C^1 complex **49**. Similarly, in the corresponding transition states these distances are 2.217 and 1.598 Å, respectively (Figure 7).

Conclusions

Several conclusions of interest for the bromination mechanism[6] of these highly strained methylenecyclopropanes and their spiroannelated analogues emerge from the comparison of the kinetic, product, and computational studies.

(1) Strain does not contribute much to the reactivity and to the product formation. The rates are neither markedly smaller nor markedly larger than those observed for acyclic methylethylenes. The rearranged products expected from a significant strain release are either absent or formed in amounts similar to those of the unrearranged products (Table 4).

(2) The rate-limiting step of the bromination is the formation of the unsymmetrical bromonium ions, not the product-forming step. The small barrier calculated for the trapping of intermediate **1·Br**$^⊕$ (Figure 6c) and the relatively small positive charge on the bromine atom argue against the possibility that the product-forming step (i.e., return) is rate limiting.[49−51]

(3) The transition states of the rate-limiting formation of the ionic intermediates are very early, resembling more the initial states than the unsymmetrical bromonium ions in which the strain could be released. This conclusion is supported by the small *m* values and KSIEs[31] (Table 3) found for the reaction of most cyclopropanated alkenes. It is also supported by the comparison of the correlations between rates and calculated energies of the bromonium ions (eq 4 and Figure 3) and those between rates and ionization potentials (eqs 6 and 7, Figure 5). In particular, the fact that the bromination rates correlate fairly well with IEs implies no change in strain energies on going from the initial to transition states because IE measures a vertical process in which changes in geometry are minimal. Charge development, "less than normal", in early transition states has been suggested previously for the solvolysis of cyclopropyl triflates[32] on the basis of their *m* values, as unusually small as those observed here for bromination of analogous substrates. This interpretation agrees with our conclusion.

(4) Nucleophilic solvation of the rate-limiting transition states[6c,51] is supported by all the kinetic, product, and computational results. The very large stabilization afforded by water complexation of the bromonium ion suggests that the reaction pathway does not go through unsolvated, naked ions but goes directly from the alkenes to the solvated intermediates. This implies that the solvent participates nucleophilically in their formation. The never large amount of rearranged products also supports the solvent participation. The methanol trapping of the intermediates is fast as compared to their rearrangement, showing that methanol is involved in the kinetically formed intermediate. These solvated intermediates are, therefore, very short-lived. Rearrangement is observed only when the positive charge is delocalized into cyclopropyl rings, as, for example, with **3** and **4**. Moreover, the small but significant rearrangement for the bromination of **1** in pentane but not in methanol (Scheme 1) is another support for the contribution of nucleophilic solvation in the formation of the corresponding ionic intermediate. All these results are consistent with the small kinetic solvent effects, observed in bromination and in solvolysis of these alkenes.

(5) The absence of a significant contribution of the strain energies of these strained alkenes to their reactivities and to their product formation[52] results mainly from the nucleophilic assistance of the solvent in the formation and the reaction of the unsymmetrical bromo-

(49) (a) Slebocka-Tilk, H.; Gallagher, D.; Brown, R. S. *J. Org. Chem.* **1996**, *61*, 3458−3466. (b) Slebocka-Tilk, H.; Motabelli, S.; Nagorski, R. W.; Turner, P.; Brown, R. S.; McDonald, R. *J. Am. Chem. Soc.* **1995**, *117*, 8769−8776.

(50) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1991**, *113*, 8012−8016.

(51) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1−67.

(52) However, the resulting products are less strained than the starting alkenes. This release of strain can be evaluated qualitatively from the known strain energies of cyclopropane (28.1 kcal/mol), and those of compounds **1** (41.7 kcal/mol), **2** (77.4 kcal/mol), and **3** (74.6 kcal/mol), assuming the validity of an additivity scheme for strain energy increments (for details see refs 2 and 3). For theoretical consideration of this question also see: Johnson, W. T. G.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 5930−5933.

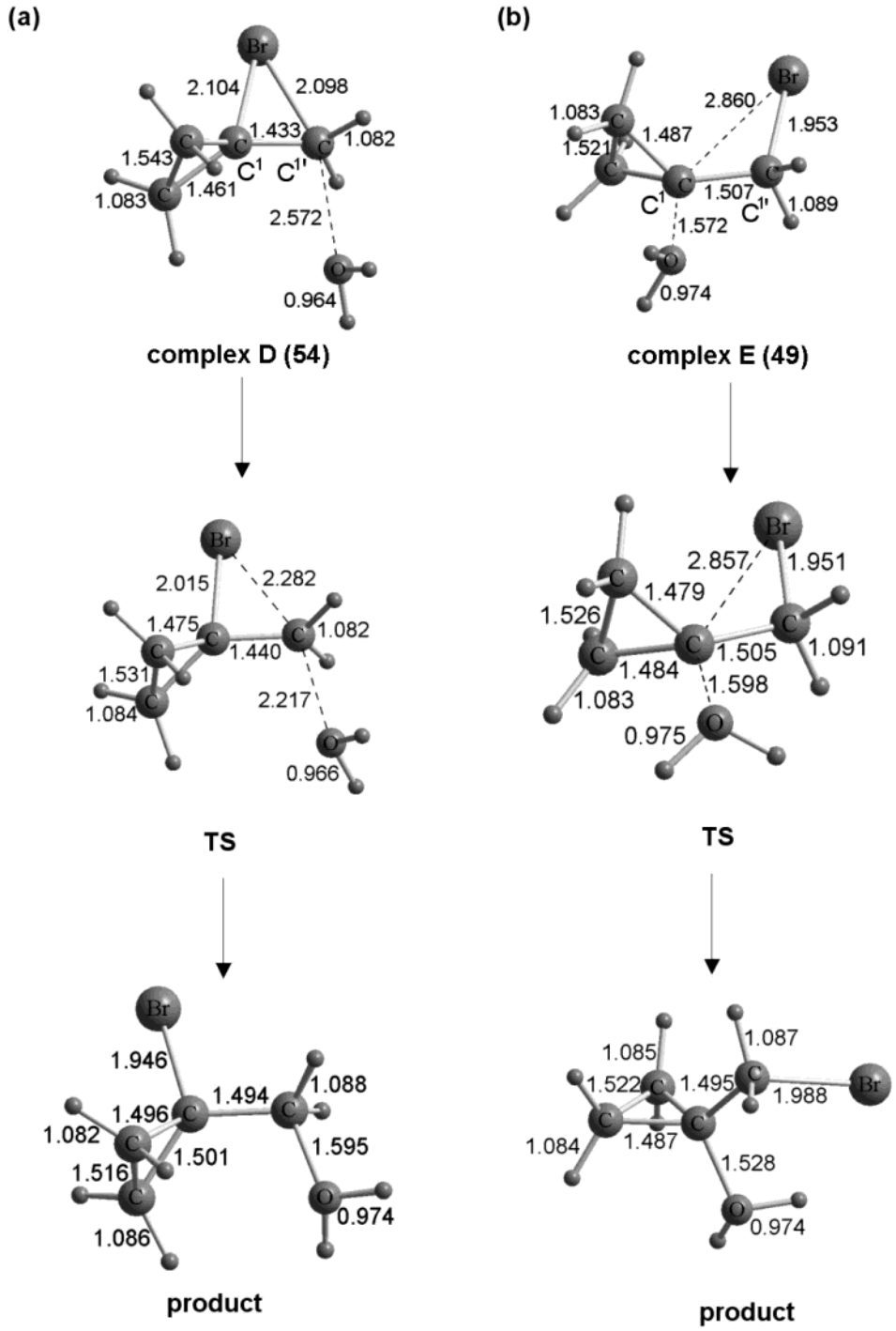


Figure 7. Calculated [B3LYP/6-311G(d,p)] geometries (bond lengths in angstroms) of bromonium ion−water complexes, transition states, and products of water attack at (a) $C^{1'}$ of **1**·**Br**$^+$ and (b) C^1 of **1**·**Br**$^+$.

nium ions and probably, but at a smaller extent, in their bromine bridging.

The successive spirocyclopropanation of the three-membered rings in **1** and **2** leads to significant stabilizations of the corresponding bromonium ion and thus to significant acceleration of the bromination reaction despite the marked increase in strain. The methylenecyclopropane (**1**, **3**, **4**, **11**, **12**) series and bicyclopropylidene (**2**, **5**, **6**) series show similar reactivity ranges for the addition of Br^+. A good linear correlation is found between the calculated stabilities of bromonium ions and the experimentally measured rates of bromination of the corresponding alkenes.

Experimental Section

General Remarks. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ solution, $CHCl_3/CDCl_3$ as internal reference, δ in parts per million, J in hertz at 250 (^{1}H) and 62.9 [^{13}C, additional DEPT (distortionless enhancement by polarization transfer)] MHz. FT-IR spectra were recorded for KBr pellets and oils between NaCl plates. MS (EI) spectra were recorded at 70 eV. Melting points are uncorrected. GC analyses were done on a 25 m capillary column CP-SIL-5-CB. TLC chromatograms were obtained using precoated sheets and 0.25 mm Sil G/UV_{254}. For chromatographic separations, silica gel 60 (230−400 mesh) was used. Anhydrous methanol was prepared by distillation from magnesium methoxide. The starting materials

Table 7. ϵ Values as a Function of the Wavelength and the Bromine Concentration

λ (nm)	solvent	[NaBr] (mol L^{-1})	ϵ (L mol^{-1} cm^{-1})
270	[D_1]methanol	0.029	30780
		0.011	41730
		0.204	43930
270	methanol	0.058	44670
		0.114	45770
		0.216	47918
345	methanol	0.056	1769
		0.105	1883
		0.208	1818

1,[5a] **2**,[53] **3**,[54] **4**,[55] **5**, **6**,[53a] **7**,[56] and **8**[57] were prepared according to reported procedures. Olefin- and water-free pentane was prepared by the common method.[58] All other chemicals were used as commercially available. Organic extracts were dried over $MgSO_4$.

Kinetic Measurements. Ethanol p.a., methanol p.a., 2,3-dimethylbut-2-ene, 99+%, and [D_1]methanol were used as commercially available. Sodium bromide (Suprapur) was dried at atmospheric pressure at 120 °C for 24 h. All solutions were used as freshly prepared within a maximum of 3 h after preparation.

1. Couloamperometric Measurements. The measuring cell (capacity about 100 mL) equipped with a motor-driven glass stirrer, electrolysis circuit, and amperometric detector circuit was used under isothermal conditions (25 ± 0.1 °C). The electrolysis circuit consisting of two Metrohm electrolysis electrodes (25 mm^2 platinum plates) was connected with a constant-current source (0.1−250 mA range) and stopwatch. The amperometric detector circuit was a three-electrode potentiostatic assembly involving a working electrode (polished platinum disks of 2 or 5 mm diameter spinning at 2000 r/min), a reference calomel electrode in satd NaCl/MeOH (EtOH) solution, and an auxiliary glass-sealed platinum electrode. The potential applied between the working and reference electrodes was that of the bromine diffusion plateau in methanol (e_{in} = +200 mV) or ethanol (e_{in} = +250 mV). The current detector circuit was a current follower amplifier with a small bias current and small false-zero potential.[14a] The output signal was registered with a recorder and oscilloscope. The cell was filled with 45−50 mL of MeOH/NaBr solution, and the potential was applied on the amperometric circuit. After thermostabilization and compensation of a residual current, the predetermined quantity of bromine was produced with the electrolysis circuit. The constant of proportionality α that varied from 12 to 47 mol·A/L in the course of measurements was averaged using the amperometric signal. Then a solution of the alkene (half as much as bromine) was injected into the cell solution. The second-order rate constant was calculated from the kinetic curve.

2. UV Spectroscopy. The measurements were performed using a spectrometer connected with data acquisition. The measuring cell of capacity 2.5 mL and 1 cm in thickness was equipped with a magnetic stirrer and thermostated. ϵ values were averaged as a function of wavelength and concentration of bromide using the prepared bromine/tribromide solution (Table 7).

The measuring cell and reference cell were filled with 2.2 mL of a corresponding NaBr/MeOH solution. After thermostabilization and calibration of absorbance to zero, Br_2 was injected by quickly dipping a capillary tube filled with a 10% solution in methanol, a corresponding Br_3^- concentration was produced, and the absorbance variations were registered. After injection of some microliters of a concentrated alkene solution, the absorbance decrease as a function of time gave the kinetic signal. For the reactions under pseudo-first-order conditions, the concentrations of the alkene exceeded those of bromine at least by a factor of 10. The exact concentration of the alkene was calculated using eq 8, where $m_{al,sol}$ is the exact quantity

$$[\text{alkene}]^0 = \frac{m_{al,sol}}{m_{al,sol} + m_{MeOH}} \frac{1}{M_a + V_{cell}} m_{inj} \qquad (8)$$

of alkene in its mother solution, m_{MeOH} the mass of methanol used in the preparation of concentrated olefin solution, M_{al} the molecular weight of olefin, V_{cell} the cell volume, and m_{inj} the injected mass of mother alkene solution. For the reactions under second-order conditions, the concentration of alkene was about half the bromine concentration. After the registration of the course of the absorbance curve, a known quantity of 2,3-dimethylbut-2-ene was added to determine the final bromine concentrations. The rate constants were evaluated from the kinetic curve.

General Procedure (GP 1) for the Addition of Bromine to Hydrocarbons 1−6 in Methanol. To a stirred solution of NaBr (3.0 g, 29.2 mmol) in anhydrous methanol (70 mL) was added bromine (4.0 g, 1.29 mL, 25 mmol) in one portion in the absence of light and moisture at 25 °C. Stirring was continued for 2 min, and then a solution of the alkene (12.5 mmol) in MeOH (2 mL) was added at the indicated temperature. After being stirred for 2 min, the mixture was poured into an ice-cold solution of $Na_2S_2O_3$ (5 g) and $NaHCO_3$ (10 g) in water (100 mL) and quickly extracted with pentane (3 × 50 mL). The combined organic phases were washed with a 5% $NaHCO_3$ solution, water, and brine before they were dried and concentrated under reduced pressure. The residue was separated by flash column chromatography (75 g of silica gel, column 30 × 3 cm). Taking into account the instability and sensitivity of the products to silica gel, their relative ratio was determined using NMR spectrometry before chromatographic separation.

1-Bromo-1-(bromomethyl)cyclopropane (20) and 1-Bromo-1-(methoxymethyl)cyclopropane (23). From methylenecyclopropane (**1**) (1.0 g, 18.49 mmol), compounds **20**[5b] (0.753 g, 19%) and **23** (0.210 g, 7%) were obtained according to GP 1 after column chromatography (eluent pentane).

Data for **20**: ^{13}C NMR δ 18.50 (2 CH_2), 43.72 (CH_2), 32.08 (C). Data for **23**: ^{1}H NMR δ 0.79−0.90 (m, 4 H, 2 CH_2), 3.40 (s, 3 H, OCH_3), 3.48 (s, 2 H, CH_2); ^{13}C NMR δ 58.69 (CH_3), 14.26 (2 CH_2), 79.76 (CH_2), 46.09 (C).

1-Bromo-1-(1′-bromocyclopropyl)cyclopropane (24), 1-(1′-Bromocyclopropyl)-1-methoxycyclopropane (25), and 1,3,5-Tribromo-2-(bromomethyl)pent-2-ene (28). From bicyclopropylidene (**2**) (1.0 g, 12.48 mmol), compounds **24** (2.115 g, 71%), **25** (0.383 g, 16%), and **28** (0.352 g, 7%) were obtained according to GP 1 after column chromatography (eluent pentane/Et_2O, 100:1). Data for

24: R_f = 0.8; mp 37−38 °C; ^{1}H NMR δ 1.02−1.08 (m, 4 H, 2 CH_2), 1.32−1.39 (m, 4 H, 2 CH_2); ^{13}C NMR δ 19.53 (4 CH_2), 41.77 (2 C); MS (EI) *m*/*z* (rel intens) 242/240/238 (M^+, 3/5/2), 214/212/210 ($M^+ - C_2H_4$, 14/30/14), 161/159 (M^+ − Br, 27/27), 133/131 (M^+ − Br − C_2H_4, 15/15), 80 ($M^+ - Br_2$, 60), 79 (100). Anal. Calcd for $C_6H_8Br_2$: C, 30.03; H, 3.36. Found: C, 30.16; H, 3.35.

Data for **25**: R_f = 0.15; ^{1}H NMR δ 0.61−0.69 (m, 2 H, CH_2), 0.81−0.88 (m, 2 H, CH_2), 0.91−0.98 (m, 2 H, CH_2), 1.16−1.23 (m, 2 H, CH_2), 3.43 (s, 3 H, OCH_3); ^{13}C NMR δ 55.05 (CH_3), 14.39, 15.26 (2 CH_2), 35.72, 66.50 (C).

Data for **28**: R_f = 0.50; ^{1}H NMR δ 3.16 (t, 2 H, J = 6.8 Hz, CH_2), 3.61 (t, 2 H, J = 6.8 Hz, CH_2Br), 4.22 (s, 2 H, CH_2Br), 4.32 (s, 2 H, CH_2Br); ^{13}C NMR δ 27.83, 28.76, 32.52, 40.69 (CH_2), 130.19, 135.16 (C).

1-Bromo-1-(bromomethyl)spiropentane (29), 1′-(Bromomethyl)cyclopropyl Bromomethyl ketone (31), and 1′-(Bromomethyl)cyclopropyl Bromomethyl Ketone Dimethyl Acetal (32). From methylenespiropentane (**3**) (1.0 g, 12.48 mmol), compounds **29** (0.825 g, 28%), **31** (0.623 g, 19%),

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and **32** (0.432 g, 12%) were obtained according to GP 1 after column chromatography (eluent pentane/Et_2O, 40:1).

Data for **29**: R_f = 0.55; ^{1}H NMR δ 0.85−1.10 (m, 3 cyclopropyl H), 1.23−1.41 (m, 1 cyclopropyl H), 1.48 (d, 1 H, J = 11.0 Hz, CH_2), 1.70 (d, 1 H, J = 11.0 Hz, CH_2), 3.69 (d, 1 H, J = 11.0 Hz, CH_2Br), 3.84 (d, 1 H, J = 11.0 Hz, CH_2Br); ^{13}C NMR δ 7.29, 8.88, 24.43, 43.84 (CH_2), 25.33, 39.64 (C).

Data for **31**: R_f = 0.15; ^{1}H NMR δ 1.13−1.21 (m, 2 H, CH_2), 1.63−1.70 (m, 2 H, CH_2), 3.74 (s, 2 H, CH_2Br), 4.20 (s, 2 H, CH_2Br); ^{13}C NMR δ 22.10 (2 CH_2), 30.67, 36.58 (CH_2), 32.54, 199.45 (C).

Data for **32**: R_f = 0.30; ^{1}H NMR δ 0.62−0.68 (m, 2 H, CH_2), 1.32−1.38 (m, 2 H, CH_2), 3.20 (s, 6 H, 2 OCH_3), 3.54 (s, 2 H, CH_2Br), 3.73 (s, 2 H, CH_2Br); ^{13}C NMR δ 48.63 (2 CH_3), 12.79 (2 CH_2), 31.70, 39.66 (CH_2), 22.42, 98.88 (C).

Dispiro[2.0.2.2]octan-7-one (33), 7-Bromo-7-(bromomethyl)-dispiro[2.0.2.1]heptane (34), and 7-(Bromomethyl)-7-methoxydispiro[2.0.2.1]heptane (35). From **4** (1.06 g, 9.98 mmol), compounds **33**[59] (0.296 g, 24%), **34** (0.375 g, 14%), and **35** (0.245 g, 11%) were obtained according to GP 1 after column chromatography (eluent pentane/Et_2O, 40:1).

Data for **33**: R_f = 0.30; ^{13}C NMR δ 8.13, 14.27 (2 CH_2), 52.69 (CH_2), 18.38, 43.08, 213.19 (C).

Data for **34**: R_f = 0.90; ^{1}H NMR δ 0.81−0.98 (m, 4 H, 2 CH_2), 1.00−1.10 (m, 2 H, CH_2), 1.20−1.38 (m, 2 H, CH_2), 3.82 (s, 2 H, CH_2Br); ^{13}C NMR δ 6.73, 8.24 (2 CH_2), 43.11 (CH_2), 28.76 (2 C), 45.86 (C); IR (film, cm^{-1}) 3072, 2988, 1421, 1229, 1162, 1012, 961, 923, 888, 711; MS (EI) *m*/*z* (rel intens) 268/266/264 (M^+, 0.3/0.7/0.3), 187/185 (M^+ − Br, 6/7), 121 (10), 106 (100), 105 (38), 91 (83), 77 (46).

Data for **35**: R_f = 0.40; ^{1}H NMR δ 0.51−0.61 (m, 2 H, CH_2), 0.79−0.88 (m, 2 H, CH_2), 1.02−1.11 (m, 2 H, CH_2), 1.12−1.21 (m, 2 H, CH_2), 3.40 (s, 3 H, OCH_3), 3.75 (s, 2 H, CH_2Br); ^{13}C NMR δ 54.92 (CH_3), 3.94, 4.95 (2 CH_2), 37.04 (CH_2), 24.63 (2 C), 64.52 (C); MS (EI) *m*/*z* (rel intens) 218/216 (M^+, 0.4/0.4), 137 (M^+ − Br, 20), 122 (M^+ − Br − CH_3, 10), 109 (M^+ − Br − C_2H_4, 38), 105 (M^+ − Br − $HOCH_3$, 98), 91 ($C_7H_7^+$, 22), 79 (100).

1-Bromo-1-(1′-bromocyclopropyl)spiropentane (36), 1-(1′-Bromocyclopropyl)-1-methoxyspiropentane (37), and 1′-Bromocyclopropyl 1′-(Bromomethyl)cyclopropyl Ketone Dimethyl Acetal (39). From cyclopropylidenespiropentane (**5**) (1.327 g, 12.5 mmol), compounds **36** (1.079 g, 32%), **37** (1.313 g, 48%), and **39** (0.600 g, 15%) were obtained according to GP 1 after column chromatography (eluent pentane/Et_2O, 40:1).

Data for **36**: R_f = 0.56; bp 50 °C (0.2 Torr); mp 28−30 °C (MeOH); ^{1}H NMR δ 0.80−1.19 (m, 4 cyclopropyl H), 1.20−1.44 (m, 5 cyclopropyl H), 1.57 (d, 1 H, J = 6.0 Hz, 1 cyclopropyl H); ^{13}C NMR δ 7.93, 8.89, 18.61, 18.92, 25.66 (CH_2), 25.20, 41.76, 48.49 (C); MS (EI) *m*/*z* (rel intens) 267/265/263 (M^+ − H, 5/10/5), 185/183 (M^+ − H − HBr, 43/38), 105 (M^+ − HBr − Br, 100), 91 (M^+ − HBr − Br − CH_2, 51), 81/79 (Br^+, 40/35). Anal. Calcd for $C_8H_{10}Br_2$: C, 36.13; H, 3.79. Found: C, 36.24; H, 3.78.

Data for **37**: R_f = 0.22; bp 90 °C (3 Torr); ^{1}H NMR δ 0.63−0.74 (m, 2 cyclopropyl H), 0.77−0.82 (m, 2 cyclopropyl H), 0.93−1.03 (m, 2 cyclopropyl H), 1.06−1.15 (m, 3 cyclopropyl H), 1.19− 1.24 (m, 1 cyclopropyl H), 3.43 (s, 3 H, OCH_3); ^{13}C NMR δ 55.03 (CH_3), 4.17, 5.05, 13.55, 15.38, 17.29 (CH_2), 21.68, 35.18, 67.39 (C); MS (CI) *m*/*z* (rel intens) 253/251 (M + NH_4^+ + NH_3, 10/10), 236/234 (M + NH_4^+, 100/100). Anal. Calcd for $C_9H_{13}BrO$: C, 49.79; H, 6.04. Found: C, 49.89; H, 6.13.

Data for **39**: R_f = 0.37; ^{1}H NMR δ 0.62−0.67 (m, 2 cyclopropyl H), 0.97−1.06 (m, 2 cyclopropyl H), 1.26−1.42 (m, 2 cyclopropyl H), 1.50−1.56 (m, 2 cyclopropyl H), 3.21 (s, 6 H, 2 OCH_3), 3.63 (br s, 2 H, CH_2Br); ^{13}C NMR δ 49.14 (2 CH_3), 13.62, 14.11, 17.62, 19.28, 40.57 (CH_2), 23.53, 33.07, 98.25 (C); MS (EI) *m*/*z* (rel intens) 330/328/326 (M^+, 0.3/0.6/0.3), 316/314/312 (M^+ − CH_2, 2/4/2), 299/297/295 (M^+ − OCH_3, 49/100/50).

7-Bromo-7-(1′-bromocyclopropyl)dispiro[2.0.2.1]heptane (40) and 7-(1′-Bromocyclopropyl)-7-methoxydispiro-[2.0.2.1]heptane (41). From 7-cyclopropylidenedispiro[2.0.2.1]-heptane (**6**) (1.0 g, 7.56 mmol), compounds **40** (0.204 g, 9%) and **41** (0.849 g, 46%) were obtained according to GP 1 after column chromatography (eluent pentane/Et_2O, 40:1).

Data for **40**: R_f = 0.85; bp 80 °C (0.2 Torr); mp 83−85 °C [MeOH, then sublimation at 80 °C (0.2 Torr)]; ^{1}H NMR δ 0.75−0.83 (m, 2 H, CH_2), 0.95−1.00 (m, 4 H, 2 CH_2), 1.20−1.25 (m, 2 H, CH_2), 1.27−1.37 (m, 4 H, 2 CH_2); ^{13}C NMR δ 7.68, 8.31, 18.04 (2 CH_2), 28.17 (2 C), 42.29, 54.70 (C). Anal. Calcd for $C_{10}H_{12}Br_2$: C, 41.13; H, 4.14. Found: C, 41.23; H, 4.12.

Data for **41**: R_f = 0.35; bp 55 °C (0.2 mm); mp 24−25 °C (pentane); ^{1}H NMR δ 0.60−0.74 (m, 4 H, 2 CH_2), 0.98−1.05 (m, 2 H, CH_2), 1.05−1.15 (m, 4 H, 2 CH_2), 1.17−1.23 (m, 2 H, CH_2), 3.45 (s, 3 H, OCH_3); ^{13}C NMR δ 54.94 (CH_3), 4.17, 4.87, 14.41 (2 CH_2), 23.33 (2 C), 35.46, 74.20 (C); MS (CI) *m*/*z* (rel intens) 279/277 (M + NH_4^+ + NH_3, 8/8), 262/260 (M + NH_4^+, 100/100), 230/228 (M^+ − CH_2, 4/4). Anal. Calcd for $C_{11}H_{15}BrO$: C, 54.34; H, 6.22. Found: C, 54.61; H, 6.27.

7-Bromo-7-cyclopropyldispiro[2.0.2.1]heptane (42) and 7-(1′-Bromocyclopropyl)dispiro[2.0.2.1]heptane (43). To a stirred solution of **6** (200 mg, 1.51 mmol) in olefin- and water-free pentane (50 mL) was added a 0.3 M solution of HBr in pentane (10 mL, 3 mmol) over 30 min at −30 °C. The reaction mixture was stirred over a period of 1 h and treated with $NaHCO_3$ (500 mg) at this temperature. 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 **42** and **43** as a 10:1 mixture that could hardly be separated because compounds **42** and **43** were unstable toward silica gel.

Data for **42**: ^{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); ^{13}C NMR δ 4.78, 7.81, 7.83 (2 CH_2), 25.21 (CH), 19.62 (2 C), 51.73 (C); IR (film, cm^{-1}) 2940, 2860, 2800, 1015, 820, 770, 750, 635; GC−MS (EI) *m*/*z* (rel intens) 213/211 (M^+ − H, 0.3/0.3), 131 (M^+ − H − HBr, 9), 117 (34), 105 (M^+ − Br − C_2H_4, 83), 79 (33), 69 (100).

Data for **43**: ^{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); ^{13}C NMR δ 7.82 (4 CH_2), 4.71 (2 CH_2), 25.25 (CH), 19.59 (2 C), 51.60 (C).

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Supporting Information Available: Fully optimized Cartesian coordinates of structures **1**−**19** and **1**·Br^+−**19**·Br^+, their calculated total and zero-point vibrational energies, and a figure of the fully optimized important geometrical parameters of structures **1**−**19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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