J mol^{-1} K^{-1}) and of ferrocenylmethyl benzoate (−25 J mol^{-1} K^{-1}) are generally expected in reactions proceeding with neighboring group participation. For example, it has been concluded that the assisted solvolyses tend to have $\Delta S^{\ddagger}$ of about −30 J mol^{-1} K^{-1}, as it is the case in formolysis of 2-phenylethyl tosylate,[25] where $\Delta S^{\ddagger}$ = −40 J mol^{-1} K^{-1}. In the case of more reactive 2,2-dimethyl-2-phenylethyl tosylate $\Delta S^{\ddagger}$ is −31, −23, and −26 J mol^{-1} K^{-1} in ethanol, acetic acid, and formic acid, respectively.[25]

Experimental Section

Preparations. Ferrocenylmethyl acetate was obtained from (ferrocenylmethyl)trimethylammonium iodide, via carbinol,[26] by the method previously published;[27] mp 68–69 °C; ν(CO) 1750 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}O_2Fe$: C, 60.28; H, 5.73; Fe, 21.58. Found: C, 60.50; H, 5.43; Fe, 21.32 (gravimetrically).

Ferrocenyldideuteriomethyl acetate was prepared in the same way as the undeuterated compound, but by using D_3PO_4, NaOD, CH_3COOD, D_2O (Merck, 99,8 %), and bis(dimethylamino)dideuteriomethane[28] instead of undeuterated material. The NMR spectra showed that the deuteration was essentially complete.

Ferrocenylmethyl benzoate was prepared from the corresponding carbinol with benzoyl chloride in pyridine by using a general procedure;[29] mp 130–132 °C; ν(CO) 1745 cm^{-1}.

Anal. Calcd for $C_{18}H_{16}O_2Fe$: C, 67.52; H, 5.04; Fe, 17.44. Found: C, 67.31; H, 5.27; Fe, 17.22.

Ferrocenyldideuteriomethyl benzoate was prepared from deuterated carbinol as described for the undeuterated compound. All preparations were carried out in an argon atmosphere to avoid the formation of ferricynium salts.[30]

The chemicals used, including deuterated compounds, were from Merck and of analytical purity. D_2CO, needed for preparation of bis(dimethylamino)dideuteriomethane[28] was supplied as 30% (v/v) solution of 99% D_2CO in D_2O (99.8%), stabilized by deuterated methanol.

Kinetics. Solvolyses of ferrocenylmethyl acetate and benzoate as well as solvolyses of their deuterated analogues were carried out in 96% (v/v) ethanol. The weighed quantity of the complex was dissolved in ethanol thermally equilibrated at desired temperature (±0.02 °C). Aliquots were withdrawn at suitable intervals, quenched by 10-fold dilution with ice-cold ethanol, and titrated with standardized sodium hydroxide solution, with phenol red indicator. A stream of argon was passed through the quenched solution for about 5 min to eliminate carbon dioxide and during titration only over the surface of the reaction solution. First-order rate constants were calculated by using a nonlinear regression analysis computer program[31] on a PDP 8/e computer.

Apparatus. ^{1}H NMR spectra were recorded on a Varian 60 Mc ^{1}H NMR spectrometer, and IR spectra on a Perkin-Elmer 457 IR spectrophotometer.

Acknowledgment. We thank Professor Maurice M. Kreevoy for helpful discussions.

Registry No. D_2, 7782-39-0; $FcCH_2OAc$, 12300-24-2; $FcCH_2O_2CPh$, 12300-31-1.

(25) Winstein, S.; Heck, R. *J. Am. Chem. Soc.* **1956**, *78*, 4801.
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(31) Private communication by P. Kaluderčič, Faculty of Machinery Engineering, University of Sarajevo, in press.

Cationic Derivatives of Bicyclo[4.2.1]nona-2,4,7-triene as Model Systems for Ground-State Möbius Aromaticity†

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A number of syn-C_{10} carbocations of bicyclo[4.2.1]nona-2,4,7-triene 1 are described, furnishing possible model systems for the investigation of ground-state Möbius aromaticity. Sign inversion, necessary for 4-π-electron aromaticity, is realized by a simple orientation of the C_{10} p orbital which is homoconjugated with $C_{2,5}$. ^{13}C and ^{1}H NMR spectroscopy suggest that the empty orbital at C_{10} is orientated perpendicularly with respect to the mirror plane of the cations. The saturated analogues of these cations also adopt this configuration. The chemical shift differences between the unsaturated cations and the saturated derivatives suggest a charge delocalization via Möbius aromaticity.

A concept which has been of special interest for organic chemists is the Hückel rule,[1] which says that for ground-state molecules with a cyclic array of atomic orbitals, $4n + 2$ electrons result in aromaticity and thermodynamical stability. Fundamental in Hückel's reasoning is the large energy difference between the ground-state and the excited state(s) in a ring with $4n + 2$ electrons, whereas $4n$ electrons result in a small energy separation. The same is also true for a cyclic array of orbitals with $4n$ and $4n + 2$ electrons, respectively, when this interchange is accompanied with an odd number of sign inversions for the orbitals in the ring.[2] In the latter case, we are generally speaking of Möbius aromaticity: $4n$ electrons result in aromaticity. By use of simple MO calculations, the Möbius aromaticity concept has been explored for a variety of reactions, which are commonly known as Woodward–Hoffmann reactions.[3,4] Ground-state Möbius aromaticity has never been observed as a consequence of the steric strain, which imposes a sign inversion on a small cyclic

†This work was abstracted from the Ph.D. dissertation of H.M.J.G., Eindhoven University of Technology, Eindhoven, The Netherlands, 1982.

(1) Hückel, E. *Z. Phys.* **1931**, *70*, 204.
(2) (a) van der Hart, W. J.; Mulder, J. J. C.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 5724. (b) Zimmerman, H. E. *Tetrahedron* **1982**, *38*, 753.
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(4) (a) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1564. (b) Zimmerman, H. E. *Acc. Chem. Res.* **1971**, *4*, 272. (c) Dewar, M. J. S. *Angew. Chem.* **1971**, *83*, 859.

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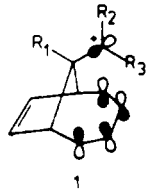
polyene. One possible way to generate ground-state $4n$-electron aromaticity is the preparation of dihomocyclic systems **1**. Sign inversion may then be realized by a simple



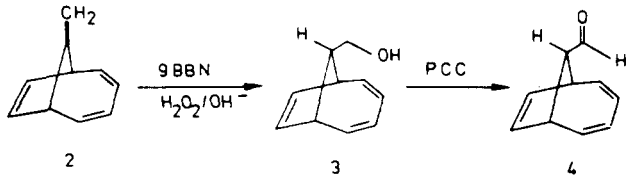
1

orientation of the C_{10} p orbital, which is homoconjugated with $C_{2,5}$. In fact, this resembles the transition state for the thermal [1,3]C and [1,4]C sigmatropic shifts.

We will describe the generation and investigation of α-heterosubstituted C_{10} cations. ^{13}C and ^{1}H NMR spectroscopy suggest that the empty orbital at C_{10} is orientated perpendicularly with respect to the mirror plane of the cations. The saturated analogues of these cations also adopt this configuration. The chemical shift differences between the unsaturated cations and the saturated derivatives can be explained by charge delocalization via Möbius aromaticity.

Synthetic Considerations

Hydroboration of 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (**2**) with 9-borabicyclo[3.3.1]nonane (9-BBN) occurs

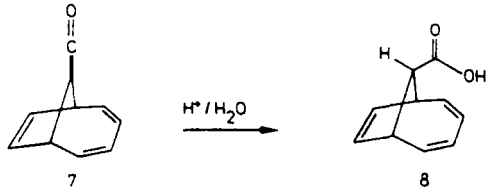


2 **3** **4**

at the anti side. Oxidation yields alcohol **3**; further oxidation with pyridinium chlorochromate (PCC) affords aldehyde **4**. The overall yield of this reaction sequence is about 9% because of the reluctancy of **2** in the hydroboration reaction and the occurrence of oxidative cleavage in the oxidation of **3**. This indicates that the direct introduction of a functionalized carbon chain[5] is to be preferred over a divergent reaction route. The logical starting compound for such an approach is bicyclo[4.2.1]nona-2,4,7-trien-9-one (**5**). Various β-heterosubstituted deriv-

5 **6**

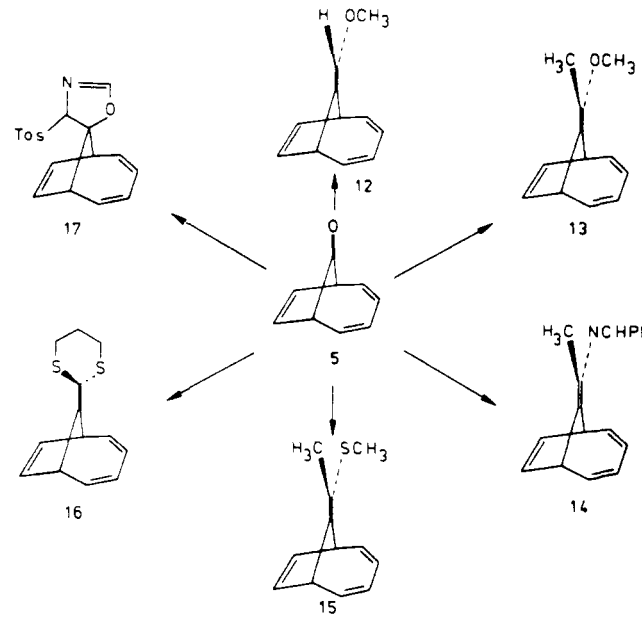
atives **6** are obtainable upon the reaction of **5** with suitably functionalized carbanions. Acidic hydrolysis of **6** would afford aldehydes, ketones, and carboxylic acid derivatives. However, in order for one to obtain model systems for the investigation of Möbius aromaticity, the protonation step of the hydrolysis reaction has to proceed from the anti direction. It is known that the hydrolysis of ketene **7**



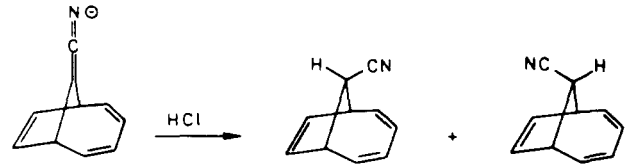
7 **8**

(5) For a recent review see: Martin, S. F. *Synthesis* **1977**, 633.

Scheme I



proceeds with 100% stereospecificity to produce carboxylic acid **8**.[6] The carbanion **9** reacts with HCl at 0 °C to produce the two epimeric nitriles **10** and **11**. At −80 °C,

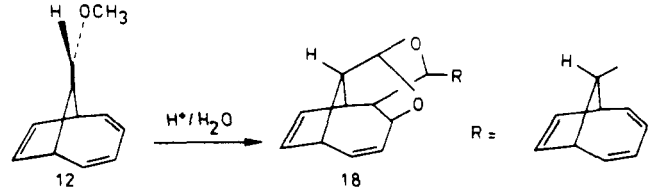


9 **10** **11**

only anti-protonated nitrile **10** is formed.[7] These results make it clear that anti protonation of sp^2-hybridized heterosubstituted derivatives of bicyclo[4.2.1]nona-2,4,7-triene (**6**) is definitely favored over syn protonation. Thus, the synthetic approach to model system **1** (R_1 = H) via hydrolysis of compounds **6** is fully supported by the available experimental evidence.

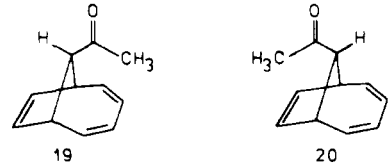
The synthesis of various potentially useful derivatives of type **6** is depicted in Scheme I.

Hydrolysis of vinyl ether **12** affords under special reaction conditions low yields of aldehyde **4**. Under normal conditions, dimeric product **18** is formed.[8]



12 **18**

Compounds **13**–**15** are precursors for the synthesis of ketone **19**. This ketone is produced in good overall yield



19 **20**

(6) (a) Zimmerman, H. E. *J. Org. Chem.* **1955**, *20*, 549. (b) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1968**, *90*, 6091. (c) Press, J. B.; Shechter, H. *J. Org. Chem.* **1975**, *40*, 2446.

(7) Boche, G.; Martens, D. *Chem. Ber.* **1979**, *112*, 175.

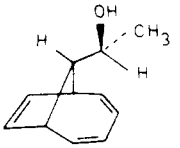
(8) Dimeric product **18** is also formed by the reaction of aldehyde **4** with 60% aqueous $HClO_4$.

Table I. Stereochemistry of Protonation

substrate	temp, °C	distribution,[a] % anti	% syn	reaction cond
7[6]	b	100	0	dioxane/water
9[7]	0	65	35	HCl/THF
	−80	100	0	HCl/THF
12	0	100	0	HCl/PhSH/$CHCl_3$
	20	100	0	$HClO_4$/water[d]
	−80	100	0	CF_3COOH/SO_2
13	20	100	0	$SiO_2/CHCl_3$[c]
14	20	85	15	$SiO_2/CHCl_3$[c]
	20	85	15	$(COOH)_2$/MeOH/H_2O
15	0	0	100	EtSH/HCl/$CHCl_3$
24	20	100	0	$HClO_4/H_2O$[d]
25	20	85	15	$SiO_2/CHCl_3$[c]
26	0	0	100	EtSH/HCl/$CHCl_3$

[a] Refers to side of protonation. [b] Not specified. [c] Hydrolysis upon chromatography. [d] Yields a dimeric Prins product.

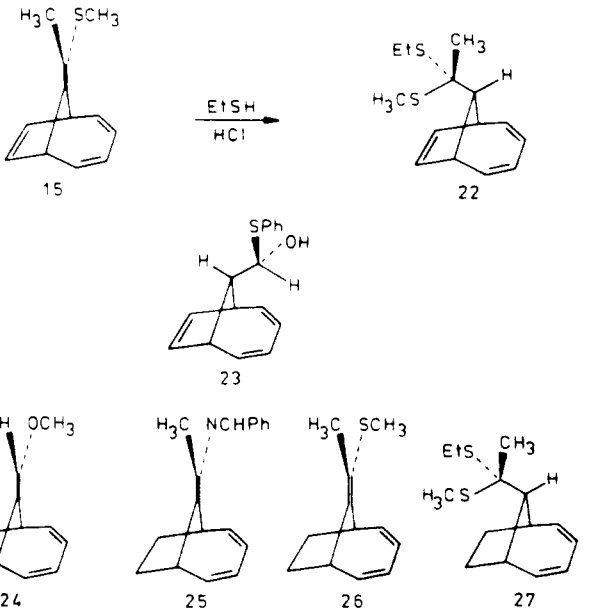
by the hydrolysis of enamine **14**. Epimeric ketone **20** is also isolated. Under identical experimental conditions vinyl ether **13** affords exclusively ketone **19**. Transition-metal-induced hydrolysis[9] of vinyl sulfide **15** is unsuccessful. Ketene thioacetal **16** is also resistent to metal-induced hydrolysis. However, oxazoline **17** is easily converted in carbonitriles **10** and **11**, thus making carboxylic acid derivatives of bicyclo[4.2.1]nona-2,4,7-triene available. The β-heterosubstituted olefins **12–15** can be used directly as precursors for model systems possessing ground-state Möbius aromaticity. Upon protonation these compounds produce α-heterosubstituted cations. α-Heterosubstituted cations are also available via protonation of the carbonyl functionality of the carbonyl compounds **4** and **19**. Finally, the carbonyl compounds **4** and **19** can be reduced to the alcohols **3** and **21**. These alcohols may serve as precursors for the generation of carbocations.



21

Stereochemistry of Protonation

The transition-metal-induced hydrolysis of vinyl sulfide **15** is unsuccessful. However, vinyl sulfides can be converted to thioketals when reacted with thiols in the presence of dry HCl.[10] Reaction of **15** with ethanethiol results in the formation of thioketal **22**. Under identical conditions, vinyl ether **12** reacts with a thiol to produce the hemithioketal **23**. The syn protonation of vinyl sulfide **15** is a very surprising result in view of the predominant or even exclusive anti protonation of other β-heterosubstituted derivatives **6** (vide infra). Table I displays data on the stereochemistry of protonation[11] of various trienyl derivatives **6**. Data with respect to the side of protonation of the dienyl derivatives **24–26** are included in Table I.

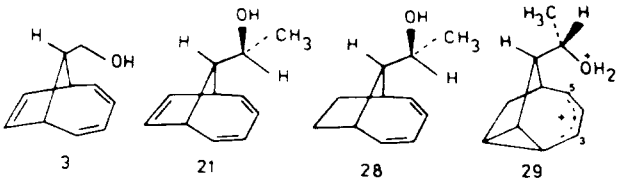


These data indicate that the aberrant protonation of **15** cannot be attributed to the presence of the etheno bridge in **15**. Vinyl sulfide **26** yields upon protonation in the presence of ethanethiol the syn-protonated product **27**. The other compounds display the expected behavior (vide infra). Thus, the presence of the etheno bridge in compounds **12–15** has no influence on the stereochemistry of protonation.

The acid-catalyzed hydrolysis of numerous vinylic substrates has been thoroughly investigated in recent years.[12-14] It has been established that the reaction proceeds via rate-determining and irreversible protonation of the olefinic linkage. The quench results of the carbanion **9**[7] make it clear that anti approach of the proton is favored over syn approach. Other evidence confirms this conclusion (see Table I). Anti protonation yields α-heterosubstituted cations, which may be stabilized by Möbius aromaticity. The intermediate cations are investigated with the aid of NMR spectroscopy. The protonation of vinyl sulfide **15** is included in this study in order to obtain an answer for the aberrant syn protonation.

NMR Spectroscopic Investigations of Cations under Long-Life Conditions

Möbius aromaticity should be reflected in the NMR spectral parameters of the carbocationic model system **1** (R_1 = H). Therefore, precursors to model system **1** (R_1 = H) were investigated in superacid media with the aid of ^1H and ^{13}C NMR spectroscopy. Alcohols **3**, **21**, and **28** are



precursors for the generation of carbocations. Addition

(9) For a recent review see: Gröbel, B. T.; Seebach, D. *Synthesis* **1978**, 357.

(10) (a) Geiss, K. H.; Seuring, B.; Pieter, R.; Seebach, D. *Angew. Chem.* **1974**, *86*, 484. (b) Mura, A. J.; Matejich, G.; Grieco, P. A.; Cohen, T. *Tetrahedron Lett.* **1975**, 4437. (c) Geiss, K. H.; Seuring, B.; Seebach, D. *Chem. Ber.* **1977**, *110*, 1833.

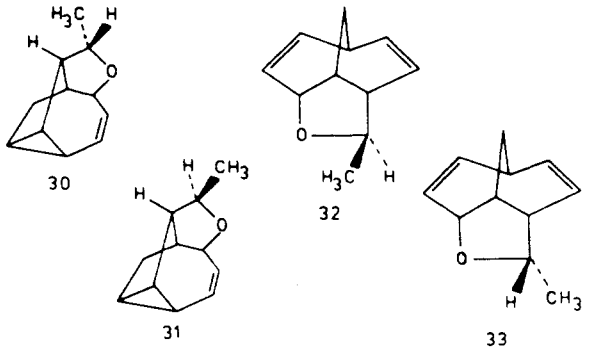
(11) The assignment is based on the multiplicity of the H_9 resonance in the ^1H NMR spectrum. Further evidence comes from ^1H NMR homodecoupling experiments.

(12) (a) Woods, D. M.; Jones, N. F. *J. Chem. Soc. B* **1964**, 5400. (b) Kresje, A. J.; et al. *J. Am. Chem. Soc.* **1971**, *93*, 413; **1972**, *94*, 2814, 2818; **1973**, *95*, 803; **1977**, *99*, 802, 805, 7228; **1978**, *100*, 1249.

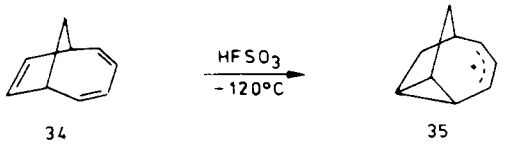
(13) (a) Okuyama, T.; Nakada, M.; Fueno, T. *Tetrahedron* **1976**, *32*, 2249. (b) McClelland, R. A. *Can. J. Chem.* **1977**, *55*, 548. (c) Okuyama, T.; Massago, M.; Nakkada, M.; Fueno, T. *Tetrahedron* **1977**, *33*, 2249.

(14) (a) Stamhuis, E. J.; Maas, W. *J. Org. Chem.* **1965**, *30*, 2156. (b) Stamhuis, E. J.; Maas, W.; Wijnberg, H. *Ibid.* **1965**, *30*, 2160. (c) Maas, W.; Janssen, M. J.; Wijnberg, H. *Ibid.* **1967**, *32*, 1111.

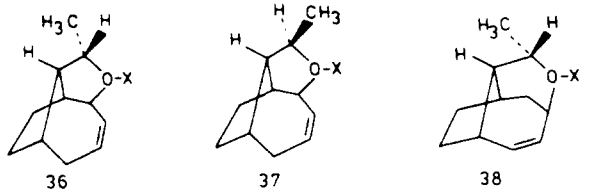
of $HFSO_3$ to a solution of **3** in SO_2ClF at −78 °C leads to protonation of the hydroxyl group. This follows directly from the downfield shift of the α-protons. Dehydration of protonated **3** in excess acid initiates extensive rearrangement reactions via a prior [1,2] hydrogen shift from C_9 to C_{10}.[15] Protonation of the hydroxyl group is also observed upon the addition of $HFSO_3$ to a solution of alcohol **21** in SO_2/SO_2ClF. Excess acid leads to the formation of an allylic cation **29** (the signals for the allylic protons H_3–H_5 appear in between 8.0 and 10.3 ppm). ^{13}C NMR spectroscopy supports this assignment (resonances for the allylic carbons C_{3-5} at 207.6, 184.9, and 182.4 ppm). Inverse addition of **21** to a solution of excess $HFSO_3$ in SO_2/SO_2ClF yields the same allylic cation **29**. Quenching confirms that **21** affords an allylic cation. After the addition of a cooled solution of sodium methoxide in methanol, the tetracyclic ethers **30** and **31** are isolated. These



results are in agreement with the reported generation of an allylic cation **35** upon protonation of bicyclo[4.2.1]-nona-2,4,7-triene (**34**).[16] Tricyclic ethers **32** and **33** are



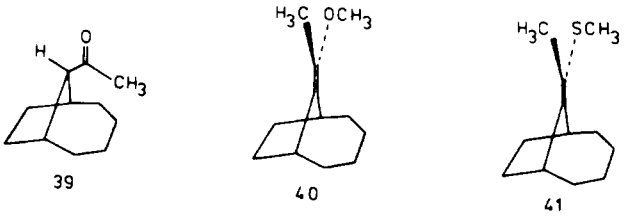
produced upon pouring the carbocationic solution onto saturated aqueous sodium bicarbonate. This is the result of an intramolecular carbon rearrangement of the cation **29**. Alcohol **28** produces upon protonation with excess $HFSO_3$ a mixture of the oxonium ions **36a**–**38a**. This



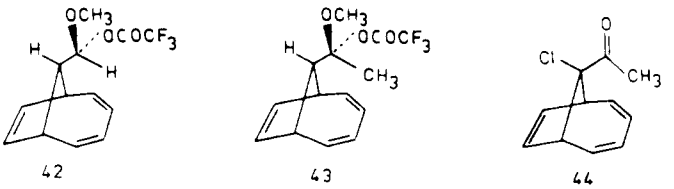
a X=H; O positively charged

b X=lone pair

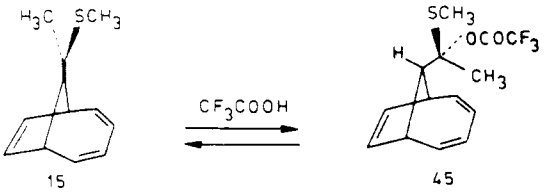
follows directly from the ^1H and ^{13}C NMR spectra. Quenching affords the tricyclic ethers **36b**–**38b**. Thus, the protonation of the diene bridge yields an allylic cation, which reacts *intra*molecularly with the hydroxyl group to produce oxonium ions. The preference for the formation of allylic cations over dehydration products with the substrates **21** and **28** precludes the investigation of a possible Möbius interaction in C_{10} carbocations. However, α-heterosubstituted cations are readily produced upon protonation of vinylic substrates **12**–**15** or upon protonation of the carbonyl functionality of carbonyl compounds **4** and **19**. Therefore, these compounds were studied under long-life conditions. The saturated substrates **39**–**41** are included in this study as reference compounds.



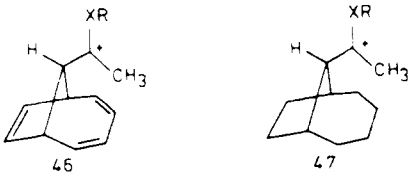
Addition of $HFSO_3$ to a solution of vinyl ether **12** in SO_2ClF leads to extensive polymerization. Aldehyde **4** also polymerizes under these conditions. Vinyl ether **12** reacts with the more nucleophilic CF_3COOH to produce the ester **42**, which is stable in an SO_2ClF solution. Quenching with aqueous sodium bicarbonate affords aldehyde **4**.



Vinyl ether **13** reacts with SO_2ClF. After quenching and workup the α-chloro ketone **44** is isolated.[17] The reaction of **13** with CF_3COOH in liquid SO_2 leads to the formation of the ester **43**. Vinyl sulfide **15** also reacts with SO_2ClF.[18] Protonation with excess CF_3COOH in SO_2 leads to the formation of ester **45**, which is in equilibrium with the



starting compound **15**. This follows directly from the temperature dependence displayed by the ^1H NMR spectrum. Thus, the protonation of vinyl sulfide **15** is reversible.[19] Upon reaction with $HFSO_3/SbF_5$ (5:1), the substrates **13**, **15**, **19**, and **39**–**41** all generate cationic solutions. The ^{13}C and ^1H NMR chemical shifts for the resulting cations **46** and **47** are collected in Tables II and III, respectively (vide infra). The chemical shifts of the ketones **19** and **39** are included.



a X=O R=H

b X=O R=CH_3

c X=S R=CH_3

(15) See also: Sanders, D. C.; Shechter, H. *J. Am. Chem. Soc.* **1973**, *95*, 6858.

(16) Roberts, M.; Hamberger, H.; Winstein, S. *J. Am. Chem. Soc.* **1970**, *92*, 6346.

(17) (a) SO_2ClF has found only limited applications in synthetic organic chemistry. The reaction of SO_2ClF with vinyl ethers to produce an α-chloro ketone might very well constitute a new synthetic reaction, which is characterized by mild reaction conditions and ease of workup. (b) Synthetic applications of SO_2ClF have been reported by: Olah, G. A.; et al., *Synthesis* **1980**, 659, 661; **1981**, 146.

(18) Vinyl sulfide **15** reacts with SO_2ClF. The resulting fluoro sulfinate ester is unstable. No product could be isolated after attempted chromatography on silica gel.

(19) Recently, Hevesi reported reversible protonation in the hydrolysis of vinyl selenides: Hevesi, L.; Piquard, J. L.; Wautier, H. *J. Am. Chem. Soc.* **1981**, *103*, 870.

Table II. ^{13}C NMR Chemical Shifts for Cations 46 and 47

compd	shift[a] $C_{1,6}$	$C_{2,5}$	$C_{3,4}$	$C_{7,8}$	C_9	C_{10}	CH_3	R
19	43.57	136.11	124.86	122.24	54.31	209.52	26.27	
46a	43.21	135.11	125.25	121.94	54.69	232.63	26.88	
46b	43.52	134.65	125.33	121.71	56.08	241.02	25.42	69.10
46c	44.68	134.18	127.25	122.32	58.23	256.12	24.10	30.50
39	37.44	32.58	24.88	31.74	60.54	213.91	28.73	
47a	38.13	31.27	24.42	29.50	63.09	246.41	29.50	
47b	38.58	31.86	24.72	31.45	63.96	245.89	26.30	68.69
47c	39.49	31.61	24.39	31.28	68.86	263.06	22.23	31.5

[a] All chemical shifts are reported in parts per million relative to external Me_4Si; the ^{13}C NMR spectra were recorded at 22.63 MHz; the solvent was liquid SO_2.

Table III. ^1H NMR Chemical Shifts for Cations 46 and 47

compd	shift[a] $H_{1,6}$	H_{2-5}	$H_{7,8}$	H_9	CH_3	R
19	3.37	6.33-5.60	5.19	2.95	2.05	
46a	3.77	6.58-5.83	5.40	3.77	2.73	
46b	3.87	6.50-5.87	5.33	3.87	2.96	4.72
46c	3.82	6.50-5.87	5.43	3.82	3.17	3.17
39	2.7	2.2-1.2		2.7	2.20	
47a	2.97	2.3-1.1		3.57	3.10	
47b	3.0	2.3-1.1		3.63	3.10	4.87
47c	3.1	2.5-1.2		3.37	3.25	3.25

[a] All chemical shifts are reported in parts per million relative to external Me_4Si; the ^1H NMR spectra were recorded at 60 MHz; the solvent was liquid SO_2.

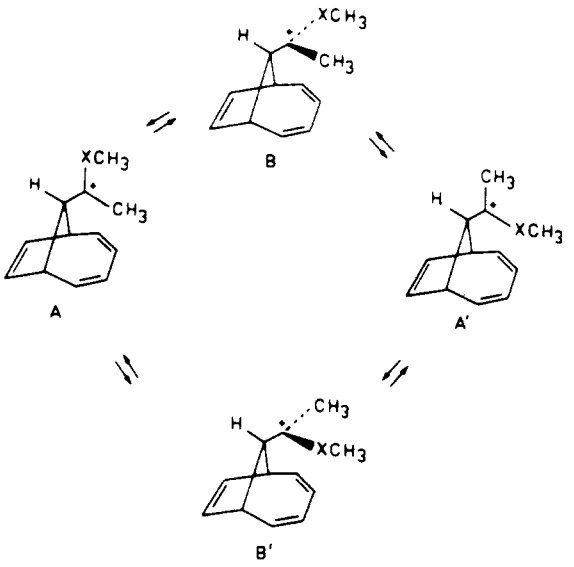
The ^1H and ^{13}C NMR spectra of cations **46** and **47** remain unchanged over a temperature range of −100 to −30 °C. This indicates that cations **46** and **47** exist in frozen configurations or that rotation around the C_9–C_{10} bond is very fast on the NMR time scale. Rotation around the C–X (X = O, S) bond is not observed. The stereochemical assignment at C_9 in cations **46c** and **47c** follows directly from the multiplicity of the H_9 resonance[20] in the 250-MHz ^1H NMR spectra. Decoupling experiments show that H_9 couples with H_1 and H_6 (J = 5.85 and 4.75 Hz in **46c** and **47c**, respectively). Furthermore, H_9 displays in both cations a long-range coupling with the methyl group (^4J = 2.0 Hz). This long-range coupling was observed over the whole temperature range of −80 to −30 °C. Its magnitude does not change upon temperature variation. No nuclear Overhauser effects are observed on H_9 upon saturation of the methyl and thiomethyl substituent, respectively. Unfortunately, during these experiments observation of the butadiene protons was omitted. Quenching of the oxygen-substituted cations affords the ketones **19** and **39**, respectively; the sulfur-substituted cations yield unreacted starting material upon quenching.

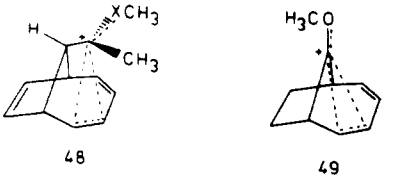
It can be concluded that α-heterosubstituted cations are readily accessible for direct NMR spectroscopic investigations. In cations **46** a Möbius-type interaction may be operative. This possibility is discussed in the next section (see Discussion). In Table II and III the ^{13}C NMR and ^1H NMR chemical shifts for cations **46** and **47** are given.

Discussion

Aromaticity and homoaromaticity are of importance in determining the stability of (homo)cyclic π-electron systems. Energy lowering of transition states and stabilization of reactive intermediates lead to enhanced reaction rates and enhanced stereospecificity, respectively. The stereochemical consequences of Möbius aromaticity in [1,3] and [1,4] carbon shifts are well-known.[21] Ground-state Möbius aromaticity has never been observed. This type of stabilization may be operative in model system 1 (R_1 = H), i.e., in the cations **46**. Upon protonation, the alcohols **21** and **28** do not form C_{10} carbocations but generate allylic cations. The introduction of α-heterosubstituents leads to stabilization of the C_{10} cations. The cations **46a–c** could be observed under long-life conditions. These cations exhibit NMR spectra which suggest a mirror symmetrical structure for the cations. The ^{13}C and ^1H NMR spectra of the cations **46** do not change over the temperature range of −100 to −30 °C. The 250-MHz ^1H NMR spectrum of cation **46c** reveals a long-range coupling between H_9 and the methyl group; the magnitude of this long-range coupling is temperature independent. From these results it is obvious that an asymmetric interaction between H_{10} and one of the double bonds of the diene moiety, as in **48**, can be excluded. This type of interaction would result in more complex NMR spectra due to the absence of a mirror plane

Scheme II





48 49

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of symmetry. An asymmetric Hückel interaction has been reported to occur in the structurally related cation **49**.[22]

The observed "symmetrical" NMR spectra may arise from frozen configurations A and A′ or via fast equilibria resulting from rotation around the C_9–C_{10} bond (see Scheme II). The configurations A and A′ have the correct geometry for the occurrence of a Möbius interaction. In saturated systems, the ^4J couplings in freely rotating fragments, e.g. CH_3–C–CH_3, are very small (ca. zero). In acyclic systems with a preferred configuration, methyl group couplings to trans- and gauche-oriented protons have coupling constants of 0.4–1.0 and 0 to –0.3 Hz, respectively. Methyl group couplings to cis-oriented protons have not been reported. However, on the basis of theoretical calculations in unstrained systems, this coupling should be approximately equal to the coupling constant between methyl groups and trans-oriented protone.[23,24] The long-range coupling between H_9 and the methyl group in cation **46c** points to configurations A and A′ for this cation, because the methyl group is oriented trans and cis, respectively, with respect to the proton at C_9. Free rotation around the C_9–C_{10} bond should result in a very small coupling constant (vide supra). The saturated cations **47a–c** also display NMR spectra which suggest a symmetrical structure for the cations. Similarly, the 250-MHz ^1H NMR spectrum of **47c** shows a temperature-independent long-range coupling constant between H_9 and the methyl group. Thus, one could conclude that cation **47c** also exists in a mirror symmetrical configuration similar to configurations A and A′. However, the C–X (X = O, S) bond in cations **46** and **47** has partial double bond character. Freely rotating species like acetone, in which the bonding situation is comparable to that in cations **46** and **47**, also display long-range coupling constants (0.54 Hz in the case of acetone[25]). So, it must be concluded that it is impossible to deduce from the observed spectral characteristics of cations **46** and **47** whether these cations are freely rotating or whether they exist in frozen configurations like A and A′ (see Scheme II). This interchange will be controlled by the configurations B and B′ which are more or less stabilized in a Hückel fashion via, e.g., **48** (compared with **49**[22]). Generally, protonation of aliphatic ketones induces a downfield shift of the carbonyl carbon of approximately 30–40 ppm.[26] For aryl ketones, smaller downfield shifts (10–20 ppm) are observed due to charge delocalization into the aryl ring(s).[26,27] The resonance of C_{10} in **46a** appears 23.1-ppm downfield with respect to the carbonyl carbon in ketone **19**. Reference compound **47a** displays a downfield shift of 32.5 ppm relative to C_{10} in ketone **39** (see Table II). The difference in the chemical shift of C_{10} between **46a** and **47a** comes to 13.8 ppm (see Table II). The shift differences between **46b** and **46c** with respect to their saturated analogues are smaller (4.87 and 6.94 ppm, respectively; see Table II). Möbius aromaticity in cations **46** should give rise to charge delocalization between C_{10} and the diene moiety and to rehybridization at C_{10}. Both charge transfer and rehybridization should result in a relative upfield shift of the cationic center with respect to the saturated analogues. So the shift differences for **46a** certainly suggest a charge delocalization via a Möbius interaction.

Experimental Section

The ^1H NMR data were obtained on Varian EM-360A, Varian T-60A, Bruker HX-90R, and Bruker WM-250 spectrometers with Me_4Si as an internal standard (δ 0.00). The ^{13}C NMR data were recorded on a Varian HA-100 or a Bruker HX-90R equipped with a Digilab FTS-NMR-3. Microanalyses were carried out in our laboratories by Messrs. P. van den Bosch and H. Eding; HPLC and GC analyses were carried out by Mr. G. Bezemer; the GC/MS spectra were recorded by Dr. P. Leclercq. The UV spectra were obtained from a Perkin-Elmer double-beam grating spectrophotometer, Model 123. Infrared spectra were recorded with a Perkin-Elmer 237 and a Beckman Acculab 9. Starting compounds 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (**2**),[28] bicyclo[4.2.1]-nona-2,4,7-trien-9-one (**5**),[20] bicyclo[4.2.1]nona-2,4-dien-9-one (**50**),[29] (methoxymethyl)diphenylphosphine oxide (**51**),[30] (1-methoxyethyl)diphenylphosphine oxide (**52**),[31] diethyl [1-(methylthio)ethyl]phosphonate (**53**),[32] diethyl [1-(benzylamino)-ethyl]phosphonate (**54**),[33] the dithioacetal of diethyl formylphosphonate (**55**),[34] are synthesized according to literature procedures. All new compounds gave satisfactory elemental analyses and/or the expected mass spectral data. ^1H and ^{13}C NMR spectral data are collected in Tables IV and V, respectively (see Appendix).

***syn*-9-(Hydroxymethyl)bicyclo[4.2.1]nona-2,4,7-triene (3).** To a solution of 1.0 g (7.7 mol) of **2** in 10 mL of dry THF was added 9-borabicyclo[3.3.1]nonane (1 equiv) under a nitrogen atmosphere. After being refluxed for 2 h, the solution was cooled to 0 °C and 0.5 mL of H_2O, 2.6 mL of 3N aqueous NaOH and 2.6 mL of H_2O_2 (30%) were added. After being stirred for 1 h, the reaction mixture was poured onto water, extracted into CH_2Cl_2, and dried ($MgSO_4$). Chromatography ($CHCl_3$–5% methanol) yielded 0.53 g (47%) of **3**, mp 58–60 °C.

***syn*-9-Carboxybicyclo[4.2.1]nona-2,4,7-triene (4).** A solution of 0.37 g (2.5 mmol) of **3** in 1 mL of CH_2Cl_2 was added rapidly to a stirred suspension of pyridinium chlorochromate (1.09 g) in 5 mL of CH_2Cl_2. After 3 h the dark-colored reaction mixture was diluted with 20 mL of Et_2O. The solvent was decanted, and the black residue was washed twice with Et_2O. The product was isolated by filtration over Florisil and concentrated. Chromatography ($CHCl_3$) yielded the product: 0.095 g (26%); IR (neat) $\nu_{C=O}$ 1730 cm^{-1}.

9-(Methoxymethylene)bicyclo[4.2.1]nona-2,4,7-triene (12). To a solution of 0.76 g of dry diisopropylamine in 15 mL of dry THF, was added 5 mL of *n*-BuLi (15% in hexane) at 0 °C under a nitrogen blanket. After 5 min, 1.86 g (7.6 mmol) of **51** was added in small portions. The resulting red solution was stirred for 10 min after the addition was completed. Then, a solution of 1.0 g (7.6 mmol) of **5** in 5 mL of dry THF was added via a dropping funnel. After being stirred for 3 h at room temperature, the reaction mixture was poured onto water and extracted into Et_2O. The organic layers were washed with water, 1 N aqueous HCl, saturated aqueous $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. Chromatography yielded 0.46 g (38%) of **12**.

Hydrolysis of 12 with Trifluoroacetic Acid. To a solution of 0.5 g (3.1 mmol) of **12** in 2 mL of $CHCl_3$ was added trifluoroacetic acid (1.5 equiv). After being stirred for 30 s, the reaction mixture was poured onto water and stirred for 1 min. The mixture was rendered alkaline by the addition of saturated aqueous $NaHCO_3$. Extraction (Et_2O), drying ($MgSO_4$), and

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chromatography ($CHCl_3$) yielded 0.13 g (30%) of **4**.

Hydrolysis of 12 with Perchloric Acid. A suspension of 0.5 g of **12**, 2 mL of Et_2O, and 2 mL of aqueous perchloric acid (65% in acid) was stirred for 15 min. After the addition of 20 mL of Et_2O, the organic phase was washed with water, saturated aqueous $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. Chromatography ($CHCl_3$) yielded pure **18**: MS, *m/e* 292; ^1H NMR ($CDCl_3$) δ 6.33–5.57 (m, 9), 5.25 (t, 2), 4.25 (t, 1), 3.6–3.0 (m, 8); ^{13}C NMR ($CDCl_3$) δ 136.1, 134.9, 133.6, 132.6, 130.8, 129.9, 126.2, 125.7, 123.8, 122.5, 100.0, 77.0, 76.2, 55.7, 49.1, 44.4, 44.1, 43.5, 40.8, 40.3.

9-(1-Methoxyethylidene)bicyclo[4.2.1]nona-2,4,7-triene (13) and *syn*-9-Acetylbicyclo[4.2.1]nona-2,4,7-triene (19). A stirred solution of 0.76 g (7.6 mmol) of diisopropylamine in 15 mL of dry THF was treated at 0 °C with 5 mL (7.6 mmol) of *n*-BuLi under a nitrogen blanket. After 10 min, 1.97 g (7.6 mmol) of **52**, dissolved in 10 mL of dry THF, was added via a dropping funnel. The ylide solution was stirred for 10 min. Subsequently, a solution of 1.09 (7.6 mmol) of **5** in THF (5 mL) was added. After the mixture was stirred for 30 min at 0 °C and 1.5 h at room temperature, the reaction was stopped by pouring the reaction mixture onto water. The reaction products were extracted in Et_2O. The combined organic layers were washed with water, dried ($MgSO_4$), filtered, and concentrated. Chromatography ($SiO_2/CHCl_3$) of the crude reaction mixture yielded pure ketone **19**, overall yield 64%. Enol ether **13** could be obtained by distillation of the crude reaction mixture. The purest fraction [bp 62–63 °C (0.6 mm)] contained approximately 5–10% of starting material **5** (GLC analysis). Alternatively, **13** can be isolated by means of chromatography (basic Al_2O_3; hexane–ethyl acetate, 85:15).

9-[1-(Benzylamino)ethylidene]bicyclo[4.2.1]nona-2,4,7-triene (14) and *syn*-9-Acetylbicyclo[4.2.1]nona-2,4,7-triene (19). To a stirred solution of 2.53 mL (3.8 mmol) of *n*-BuLi in 15 mL of dry THF was added a solution of 1.02 g (3.8 mmol) of diethyl [1-(benzylamino)ethyl]phosphonate (**54**;[33] see also the beginning of the Experimental Section) in 5 mL of dry THF with a dropping funnel at −78 °C under a nitrogen atmosphere. After 1 h, a solution of 0.5 g (3.8 mmol) of **5** in dry THF (5 mL) was added. Stirring at −78 °C was continued for 10 min. Then, the reaction mixture was allowed to warm to room temperature and refluxed for 3 h. The reaction mixture was poured onto water and extracted into Et_2O. Drying ($MgSO_4$) and concentrating yielded 1.1 g of crude aza diene **14**, which could be purified by trituration with MeOH. Hydrolysis of the aza diene was effected by passing it through a column of SiO_2 with $CHCl_3$ as the eluent. Chromatography ($CHCl_3$) afforded a mixture of **19** and **20** (55% overall yield; 85:15 ratio of **19**/**20**). Pure **19** was obtained with the aid of high-performance LC (hexane–10% ethyl acetate): IR (neat) $\nu_{C=O}$ 1715 cm^{-1}; MS, *m/e* 160; UV (MeOH) 220 nm, 257.5, 265, 276 (shoulder).

9-[1-(Methylthio)ethylidene]bicyclo[4.2.1]nona-2,4,7-triene (15). A stirred solution of 0.8 g (8.8 mmol) of diisopropylamine in 15 mL of dry THF was treated with 5.5 mL (8.25 mmol) of *n*-BuLi at 0 °C under nitrogen. After 10 min, 1.68 g (8.0 mmol) of **53**, dissolved in 5 mL of dry THF, was added with a dropping funnel. Stirring at 0 °C was continued for 4 h. Then, a solution of 1.0 g (7.6 mmol) of **5** in 5 mL of dry THF was added. The mixture was stirred for 20 h, quenched with ice-cold saturated aqueous NH_4Cl, extracted into Et_2O, washed with water, dried ($MgSO_4$), and concentrated. High-performance LC afforded 0.64 g (59%) of **15** (eluent hexane–10% ethyl acetate).

Oxazoline (17). To a stirred suspension of 0.076 g of NaCN in 15 mL of absolute EtOH was added a solution of 1.48 g of tosylmethyl isocyanide and 1.0 g (7.6 mmol) of **5** in 7 mL of dry THF under nitrogen. After 2.5 h, the solvent was stripped off, and 15 mL of CCl_4 was added. After 1 h at 0 °C the mixture was filtered. The remaining solid was recrystallized from acetone, yielding 1.87 g (76%) of **17**, mp 167 °C dec. Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23; N, 4.28. Found: C, 66.15; H, 5.40; N, 4.48.

Bicyclo[4.2.1]nona-2,4,7-triene-*syn*- and -*anti*-9-carbonitrile (10 and 11). A solution of 0.69 g of potassium *tert*-butoxide in a mixture of 5 mL of dry dimethoxyethane and 5 mL of dry *tert*-butyl alcohol was added to a stirred suspension of 1.0 g (3.1 mmol) of **17** in 20 mL of dry dimethoxyethane at 0 °C under a nitrogen atmosphere. The mixture was stirred for 0.5 h at 0 °C and 3 h at room temperature. Then, the mixture was poured onto water and extracted into Et_2O. After the extract was dried ($MgSO_4$) and concentrated, chromatography ($CHCl_3$) yielded 0.35 g (80%) of carbonitriles **10** and **11** (ratio 65:35).

9-(Methoxymethylidene)bicyclo[4.2.1]nona-2,4-diene (24). This compound was prepared and isolated as described for **12**; yield 40–70%.

9-[1-(Benzylamino)ethylidene]bicyclo[4.2.1]nona-2,4-diene (25) and *syn*-9-Acetylbicyclo[4.2.1]nona-2,4-diene (56). They are prepared and isolated as described for compounds **14** and **19**. Chromatography ($CHCl_3$) afforded pure **56**: yield 42%; mp 35–40 °C; IR (neat) $\nu_{C=O}$ 1720 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 80.92; H, 8.77.

9-[1-(Methylthio)ethylidene]bicyclo[4.2.1]nona-2,4-diene (26). This compound was prepared and isolated as described for compound **15**; yield 46%. The ^1H and ^{13}C NMR data are given in Tables IV and V, respectively.

Thioketals 22 and 27. To a solution of vinyl sulfides **15** or **26** in $CDCl_3$ was added ethanethiol (1.5 equiv). Subsequently, dry HCl gas was passed through the solution for 1 min at 0 °C. The reaction was monitored with ^1H NMR until completed. Then the mixture was poured onto saturated aqueous $NaHCO_3$ and extracted into Et_2O. After the extract was washed with brine, dried ($MgSO_4$), and concentrated, pure products were isolated with the aid of chromatography ($CHCl_3$): yields 80–98%; ^1H NMR for **22** ($CDCl_3$) δ 6.37–5.58 (m, 4), 5.07 (d, 2), 3.45 (d, 2), 2.52 (q, 2), 2.22 (s, 1), 1.97 (d, 3), 1.22 (s, 3), 1.14 (t, 3); ^{13}C NMR ($CDCl_3$) δ 136.94 ($C_{2,5}$), 124.93 ($C_{3,4}$), 121.20 ($C_{7,8}$), 64.54 (C_{10}), 51.56 (C_9), 46.51 ($C_{1,6}$), 24.25 (CH_3), 24.23 (CH_2), 15.24 (CH_3), 13.18 (CH_3); ^1H NMR for **27** ($CDCl_3$) δ 6.23–5.32 (m, 4), 3.05 (m, 2), 2.75 (s, 1), 2.62 (q, 2), 2.05 (s, 3), 2.05 (m, 4), 1.50 (s, 3), 1.18 (t, 3); ^{13}C NMR ($CDCl_3$) δ 139.50 ($C_{2,5}$), 124.12 ($C_{3,4}$), 57.14 (C_9), 65.88 (C_{10}), 43.33 ($C_{1,6}$), 24.46 (CH_3), 15.13 (CH_3), 13.40 (CH_2).

Ketene Dithioacetal 16. To a solution of 3.03 g (11.8 mmol) of **55** in 40 mL of dry THF was added 7.9 mL of *n*-BuLi at −20 °C under nitrogen. After being stirred for 30 min, the mixture was allowed to warm to room temperature, and a solution of 1.55 g (11.8 mmol) of **5** in 10 mL of dry THF was added. The mixture was stirred for one night and then poured onto water. Extraction (Et_2O), washing with water, drying ($MgSO_4$), concentration, and trituration (i-Pr_2O) yielded 1.6 g (58%) of pure **16**, mp 136–137 °C. Anal. Calcd for $C_{13}H_{14}S_2$: C, 66.61; H, 6.02. Found: C, 66.43; H, 5.98.

Hemithioketal 23. This compound was prepared and isolated as described for compounds **22** and **27**: yield 95%; ^1H NMR ($CDCl_3$) δ 7.67–7.17 (m, 5), 6.30–5.70 (m, 4), 5.30 (d, 2), 4.78 (d, 1, J = 11 Hz), 3.30 (m, 2), 3.37 (s, 1), 2.65 (dt, 1, J = 11, 6 Hz).

***syn*-9-(1-Hydroxyethyl)bicyclo[4.2.1]nona-2,4,7-triene (21).** A solution of 0.34 g (2.1 mmol) of **19** in 3 mL of dry Et_2O was dropped into a stirred suspension of lithium aluminum hydride (40 mg, 2 equiv) at 0 °C. After stirring for 2 h at room temperature, the reaction was stopped by the addition of 10% aqueous NaOH. Filtration yielded 0.32 g of crude product (mp 76–80 °C), which was purified by recrystallization from i-Pr_2O (mp 80–82 °C). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.33; H, 8.84.

***syn*-9-(1-Hydroxyethyl)bicyclo[4.2.1]nona-2,4-diene (28).** This compound was synthesized from ketone **56** as described for compound **21**. Chromatography ($CHCl_3$) followed by recrystallization from i-Pr_2O at −78 °C yielded 90% of pure product. Anal. Calcd for $C_{11}H_{16}O$ (mp 44–47 °C): C, 80.44; H, 9.82. Found: C, 80.82; H, 9.68.

Unsaturated Cyclic Ethers 30–33. A solution of **21** in dry CH_2Cl_2 was added to a stirred solution of $HFSO_3$ (3 equiv) in SO_2/SO_2ClF (1:1) at −78 °C. The reaction was stopped by pouring the reaction mixture onto saturated aqueous $NaHCO_3$ at 0 °C. The mixture was extracted into Et_2O, washed, and dried ($MgSO_4$). High-performance LC (hexane–ethyl acetate, 9:1) afforded **32** and **33** in a ratio of 2:3: ^1H NMR for **32** ($CDCl_3$) δ 6.26–5.40 (m, 4), 4.53 (dd, 1), 3.77 (dq, 1), 3.0–2.3 (m, 3), 1.78 (m, 2), 1.28 (d, 3); ^{13}C NMR δ 137.39 (d), 133.56 (d), 130.00 (d), 128.92 (d), 82.92 (d), 77.42 (d), 36.59 (d), 30.77 (t), 30.50 (d), 22.52 (q); MS *m/e* 162; UV (*c*-hexane) 223 nm; ^1H NMR for **33** ($CDCl_3$) δ 6.43–5.47 (m, 4), 4.63–4.10 (m, 2), 3.10–2.48 (m, 3), 1.78 (m, 2), 1.26 (d, 3); ^{13}C NMR ($CDCl_3$) δ 138.63 (d), 135.61 (d), 129.19 (d), 126.93 (d), 82.00 (d), 75.80 (d), 44.74 (d), 37.94 (d), 31.15 (t), 30.77 (d), 17.83 (q);

Table IV. Collected ^{1}H NMR Spectral Data

compd	chemical shift, δ				
	H_1	H_6	H_{2-5}	$H_{7,8}$	H_{others}
3	3.13 (m)		6.29-5.49 (m)	5.33 (d)	3.30 (d, 1, H_{10}), 2.25 (m, 1, H_9), 1.6 (s, 1, OH)
4	3.50 (t)		6.60-5.92 (m)	5.31 (d)	9.85 (s, 1, H_{10}), 2.91 (t, 1, H_9)
12	3.87 (d)	3.35 (d)	6.33-5.74 (m)	5.25 (d)	5.67 (s, 1, H_{10}), 3.45 (s, 3, OCH_3)
13	3.87 (d)	3.47 (d)	6.37-5.60 (m)	5.23 (d)	3.40 (s, 3, OCH_3), 1.73 (s, 3, CH_3)
14	4.37 (d)	3.72 (d)	6.40-5.50 (m)	5.30 (d)	8.00 (s, 1, N=CH), 7.8-7.1 (m, 5, Ar), 1.85 (s, CH_3)
15	3.93 (d)	3.65 (d)	6.27-5.53 (m)	5.28 (d)	2.08 (s, 3, SCH_3), 1.87 (s, 3, CH_3)
16	4.00 (d)		6.40-5.63 (m)	5.40 (d)	3.2-2.5 (m, 4), 2.5-1.87 (m, 2)
17	4.27 (m)	2.90 (m)	6.33-5.80 (m)	5.40 (m)	7.93-7.2 (AB, 4, Ar), 7.07 (d, 1, NCHO), 4.73 (s, 1, NCHC), 2.43 (s, 3, CH_3)
19	3.40 (t)		6.30-5.67 (m)	5.15 (d)	2.45 (t, 1, H_9), 2.05 (s, 3, CH_3)
20	3.40 (d)		6.40-5.65 (m)	5.13 (d)	2.50 (s, 1, H_9), 2.13 (s, 3, CH_3)
21	3.27 (m)	2.97 (m)	6.30-5.83 (m)	5.04 (d)	2.03 (dt, 1, H_9), 3.37 (dq, 1, H_{10}), 2.17 (s, 1, OH), 1.13 (d, 3, CH_3)
24	2.83 (m)	2.30 (m)	6.20-5.40 (m)	1.93 (m)	5.60 (s, 1, H_{10}), 3.53 (s, 3, OCH_3)
25	4.03 (m)	3.33 (m)	6.20-5.33 (m)	2.03 (m)	8.06 (s, 1, NCH), 7.93-7.13 (m, 5, Ar), 1.95 (s, 3, CH_3)
26	3.63 (m)	3.28 (m)	6.33-5.32 (m)	1.97 (m)	2.33 (s, 3, SCH_3), 2.17 (s, 3, CH_3)
28	2.50 (m)		6.13-5.50 (m)	1.78 (m)	2.5 (m, 1, H_9), 3.90 (dq, 1, H_{10}), 2.5 (s, 1, OH), 1.21 (d, 3, CH_3)
56	3.23-2.22 (m)		6.20-5.40 (m)	1.90 (m)	2.7 (m, 1, H_9), 2.13 (s, 3, CH_3)

Table V. Collected ^{13}C NMR Spectral Data

compd	chemical shift, δ						
	$C_{1,6}$	$C_{2,5}$	$C_{3,4}$	$C_{7,8}$	C_9	C_{10}	others
3	44.90	135.42	126.75	124.16	40.19	61.68	
4	44.41	135.45	126.39	123.10	51.64	200.11	
10	46.04	133.08	127.04	121.81	29.00		
11	48.52	134.49	125.53	121.54	33.96		
12	46.41	137.36	124.98	123.64	116.09	137.74	60.52 (OCH_3)
	43.73	137.19	124.24	123.02			
13	46.35	137.50	124.66	123.28	126.39	141.60	57.46 (OCH_3)
	44.74	136.04	125.04	123.74			14.10 (CH_3)
15	48.08	135.72	124.77	123.58	129.30	139.60	18.09 (SCH_3)
	47.16	134.05	124.28	122.83			15.45 (CH_3)
16	30.97	134.39	125.07	123.60		144.63	26.21 (CH_2), 48.42 (SCH_2)
19	44.35	135.96	125.44	122.61	54.93	206.06	27.09 (CH_3)
20	45.90	135.96	125.37	121.40	55.07	208.29	28.37 (CH_3)
21	45.33	136.45	127.31	124.46	46.80	67.33	22.89 (CH_3)
	45.24	135.25	127.09	124.37			
24	43.86	137.49	124.46	38.73	121.05	137.88	60.39 (OCH_3)
	40.80		124.11	38.56			
26	44.52	137.07	125.13	39.51	129.0	144.56	19.28 (SCH_3)
	44.09	135.29	124.45	38.80			16.21 (CH_3)
28	41.88	137.65	126.82	41.39	51.09	68.00	23.89 (CH_3)
	41.73	136.62	126.47	41.09			
39	38.91	33.83	26.05	32.90	61.71	210.30	26.97 (CH_3)
40	40.38	35.67	26.44	33.14	130.35	142.90	57.17 (OCH_3)
	38.61						14.42 (CH_3)
41	44.03	36.39	28.33	34.53	117.68	147.28	21.62 (SCH_3)
	43.36						18.57 (CH_3)
44	54.55	133.12	125.57	121.64	54.55	198.90	24.12 (CH_3
56	36.55	143.90	130.36	35.57	56.20	221.35	27.00 (CH_3)

MS (m/e) 162; UV (c-hexane) 223 nm. Quenching by adding a cooled (−78 °C) solution of $NaOCH_3$ in CH_3OH to the reaction mixture afforded after the usual workup **30** and **31**, together with a small amount of **32**. ^{1}H NMR for **30** ($CDCl_3$) δ 6.17–5.47 (d, AB, 2), 4.18 (dd, 1), 3.80 (dq, 1), 3.10–2.33 (m, 5), 1.25 (d, 3); ^{13}C NMR ($CDCl_3$) δ 130.02 (d), 125.27 (d), 78.37 (d), 77.43 (d), 53.96 (d), 47.54 (d), 29.70 (d), 27.78 (d), 25.87 (d), 22.78 (q), 21.85 (t); MS, m/e 162; ^{1}H NMR for **31** ($CDCl_3$) δ 6.12–5.57 (m, 2), 4.50–3.90 (m, 2), 3.33–2.57 (m, 2), 2.30–1.33 (m, 5), 1.22 (d, 3); ^{13}C NMR ($CDCl_3$) δ 130.02 (d), 129.00 (d), 76.65 (d), 76.50 (d), 51.16 (d), 47.73 (d), 28.96 (d), 26.70 (d), 26.51 (d), 22.54 (t), 20.19 (q); MS, m/e 162.

Unsaturated Cyclic Ethers 36–38. They are prepared and isolated as described for **30–33**. High-performance LC (hexane–ethyl acetate, 9:1) yielded the tricyclic ethers in a ratio of 2:1:1: MS (for all products), m/e 164; ^{1}H NMR for **36** ($CDCl_3$) δ 6.07–5.57 (AB, 2), 4.17 (q, 1), 4.07 (m, 1), 2.9–1.4 (m, 9), 1.28 (d, 3); ^{13}C NMR ($CDCl_3$) δ 135.70 (d), 127.21 (d), 66.80 (d), 66.28 (d), 46.01 (d), 45.14 (d), 38.84 (t), 33.23 (t), 30.08 (t), 28.19 (d), 22.36 (q); ^{1}H NMR for **37** ($CDCl_3$) δ 6.13–5.35 (d, AB, 2), 4.22 (dq, 1), 4.07 (m, 1), 3.1–1.2 (m, 9), 1.27 (d, 3); ^{13}C NMR ($CDCl_3$) δ 133.55 (d), 131.39 (d), 67.66 (d), 66.41 (d), 45.79 (d), 42.47 (d), 38.97 (t), 32.76 (t), 31.77 (t), 31.29 (d), 21.71 (q); ^{1}H NMR for **38** ($CDCl_3$) δ 5.73 (m, 2), 4.37 (m, 1), 4.17 (q, 1), 3.07–1.33 (m, 9), 1.23 (d, 3); ^{13}C NMR ($CDCl_3$) δ 132.86 (d), 130.31 (d), 77.42 (d), 73.88 (d), 55.41 (d), 46.22 (d), 37.72 (d), 34.96 (t), 32.33 (t), 23.61 (t), 22.49 (q).

9-(1-Methoxyethylidene)bicyclo[4.2.1]nonane (40) and *syn*-9-Acetylbicyclo[4.2.1]nonane (39). Compound **40** was prepared from bicyclo[4.2.1]nonan-9-one[20] and **52** as described for **13**. Distillation [bp 60–61 °C (0.6 mmHg)] afforded pure **40**, yield 78%. Compound **40** was hydrolyzed quantitatively to ketone **39** via chromatography ($SiO_2/CHCl_3$): ^{1}H NMR for **39** ($CDCl_3$) δ 2.7 (m, 3), 2.20 (s, 3), 2.2–1.2 (m, 12); ^{1}H NMR for **40** ($CDCl_3$)

δ 3.48 (s, 3), 1.80 (s, 3), 2.1-1.1 (m, 14).

9-[1-(Methylthio)ethylidene]bicyclo[4.2.1]nonane (41). This compound is prepared and isolated as described for **15**; yield 68%. Extremely pure product was obtained with the aid of high-performance LC (hexane): MS, *m/e* 196; ^{1}H NMR ($CDCl_3$) δ 3.30 (m, 1), 3.03 (m, 1), 2.20 (s, 3), 1.97 (s, 3), 2.0-1.2 (m, 12).

***syn*-9-Acetyl-9-chlorobicyclo[4.2.1]nona-2,4,7-triene (44).** To a solution of vinyl ether **13** in SO_2 at -78 °C was added an excess (3 equiv) of SO_2ClF. The reaction was instantaneous. The reaction mixture was poured onto saturated aqueous $NaHCO_3$ and extracted into Et_2O. After the extract was dried ($MgSO_4$) and concentrated, hydrolysis of the intermediate ester was effected by passing the reaction mixture through a column of SiO_2 ($CHCl_3$ as eluent): ^{1}H NMR ($CDCl_3$) δ 6.0-5.7 (m, 4), 5.30 (d, 2), 3.53 (d, 2), 2.27 (s, 3); MS, *m/e* 194, 196.

Carbocation Generation. NMR samples were prepared by condensing SO_2 from a gas cylinder into an NMR tube containing the substrate and cooled in a dry ice/acetone bath. The concentration of the samples was about 100-200 mg/0.3 mL of solvent. To the cooled solution, was carefully added freshly prepared $HFSO_3/SbF_5$ (5:1) via the wall of the tube. In the case of the unsaturated substrates **13**, **15**, and **19**, 1 equiv of acid was used; the cations **47a-c** were generated with a twofold excess of acid. Mixing was effected by shaking the samples vigorously with the aid of a vibromixer. Samples were checked with 60-MHz ^{1}H NMR spectroscopy. Spectroscopic investigations were performed in the temperature range of -100 to -30 °C. Quenching was effected by pouring the samples onto saturated aqueous $NaHCO_3$.

Appendix

Tables IV and V contain collections of various ^{1}H and ^{13}C NMR spectral data, respectively.

Registry No. **2**, 38898-39-4; **3**, 83463-30-3; **4**, 83463-31-4; **5**, 34733-74-9; **10**, 70361-08-9; **11**, 70361-10-3; **12**, 83463-32-5; **13**, 83476-30-6; **14**, 83463-33-6; **15**, 83463-34-7; **16**, 83463-39-2; **17**, 83463-35-8; **19**, 83463-52-9; **20**, 83463-53-0; **21**, 83463-42-7; **22**, 83463-40-5; **23**, 83463-41-6; **24**, 83463-36-9; **25**, 83463-37-0; **26**, 83463-38-1; **27**, 83476-31-7; **28**, 83476-32-8; **30**, 83463-43-8; **31**, 83509-96-0; **32**, 83463-44-9; **36**, 83463-45-0; **37**, 83509-97-1; **38**, 83463-46-1; **39**, 83463-47-2; **40**, 83463-48-3; **41**, 83463-49-4; **44**, 83463-50-7; **46a**, 83463-57-4; **46b**, 83463-58-5; **46c**, 83486-34-4; **47a**, 83463-54-1; **47b**, 83463-55-2; **47c**, 83463-56-3; **52**, 64304-77-4; **56**, 83463-51-8.

^{15}N NMR Spectroscopy: Prototropic Tautomerism of Azoles

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The ^{15}N NMR spectra of several azoles and their *N*-methyl derivatives were determined. The mole fractions of the NH tautomers were obtained from the ^{15}N chemical shifts of the NH tautomers and the corresponding *N*-methyl derivatives. With minor corrections in ^{15}N chemcial shifts, the *N*-methyl derivatives proved to be suitable models for the ^{15}N chemical shifts of the corresponding NH tautomers. As a result of the large chemical shift difference between the pyrrole-type and pyridine-type nitrogens, ^{15}N NMR provides a convenient, if not the most reliable, method for studying prototropic tautomerism in nitrogen heterocycles.

Introduction

Prototropic tautomerism of azoles has been extensively studied with use of NMR techniques.[1] However, in the case of ^{1}H NMR, the chemical shift substituent effect of the *N*-methyl group of the model compound is of the same magnitude as the differences in chemical shifts of the tautomeric species. Thus, interpolation between chemical shifts of the tautomeric species and the corresponding *N*-methyl model compounds is inconclusive. In a few cases low temperature[2,3] has permitted observation of the spectrum of each tautomer, which results in more definitive conclusions.

Application of ^{13}C NMR to the analysis of the tautomeric equilibria of azoles[4] by comparison of the shifts of *N*-methyl derivatives with the shifts of the tautomeric mixture is also not satisfactory. The substituent effect of the *N*-methyl is not only relatively large but sensitive to the azole. Thus, quantitative conclusions about the position of tautomeric equilibrium are usually unreliable.

Utilizing ^{14}N NMR[5] and the interpolation method to determine the position of the azole tautomeric equilibrium at first seems to be more reliable as a result of the very large chemical shift difference between the pyridine-type and pyrrole-type nitrogens. Unfortunately, the wide line widths and resulting overlapping of several different nitrogen resonances make ^{14}N NMR an unsatisfactory method.[1]

We have successfully used ^{15}N NMR and the chemical shift interpolation method to determine the position of azole tautomeric equilibria. The *N*-methyl derivatives were found to be suitable models for the corresponding tautomers. The ^{15}N spectra of the azoles exhibit the large chemical shift difference between pyridine-type and pyrole-type nitrogen atoms, but show the narrow lines expected for spin 1/2 nuclei. The narrow lines permitted the observation and assignment of a resonance for each nitrogen atom in the azoles that were studied. The ^{15}N chemical shifts for each azole and the *N*-methyl derivatives are collected in Table I.

Results and Discussion

The ^{15}N chemical shifts of the azoles collected in Table I compare favorably with the ^{14}N chemical shifts reported by Witanowski et al.[5] but only when there are two or fewer different nitrogen atoms. This is a result of overlapping of broad lines in the ^{14}N NMR spectra, which is not observed for the ^{15}N spectra. Thus, the previously reported ^{14}N chemical shifts and the ^{15}N chemical shifts are in agreement only for azoles **1-6**, **12**, **15**, **18**, and **19**.

The high-field resonance was assigned to the pyrrole-type nitrogen and the lower field resonances were assigned to the pyridine-type nitrogen atoms. The large downfield shift of the pyridine-type nitrogen atom is attributed to a large paramagnetic shielding term associated with the

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