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Antiaromatic Interaction in the 9-Methoxybicyclo[4.2.1]nona-2,4,7-trien-9-yl Cation. Evidence of Orbital Symmetry Control over 4π-Electron Interactions

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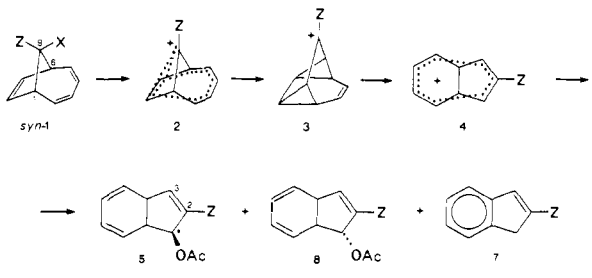
Abstract: Ionization reactions of *anti*-9-chloro-9-methoxybicyclo[4.2.1]nona-2,4,7-triene (**8**) proceed without skeletal rearrangements under conditions of short life. Rate constants were measured for the reaction of **8** and its more saturated analogues with pyridine. From the relatively low reaction rate of triene **8** it is concluded that the [4.2.1] cation is destabilized consequent to the homoantiaromatic interaction between the cationic center and the butadiene moiety. In addition to the kinetic results, the presence of this type of interaction is revealed by a NMR study of the 9-methoxybicyclo[4.2.1]nona-2,4-dien-9-yl cation (**21**) and the 11-methoxybicyclo[4.4.1]undeca-2,4,8-trien-11-yl cation (**25**) under conditions of long life, i.e., superacid media. The ^1H and ^{13}C NMR data point to an interaction of the cationic center with one of the double bonds of the butadiene moiety. Obviously the mode of homoconjugative interaction is controlled by orbital symmetry.

The theoretical analysis of bicycloaromatic stabilization in π-bridged ions by Goldstein and Hoffmann[1,2] has led to considerable effort directed toward experimental tests of their theory. In particular the bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation has evoked interest because of its stability which is expected on the basis of homoaromatic and longicyclic stabilization. Yet, the solvolysis of *syn*-bicyclo[4.2.1]nona-2,4,7-trien-9-yl *p*-toluenesulfonate (*syn*-**1a**) afforded the rearranged products *cis-exo*-dihydroindenyl acetate (**5a**) and indene (**7a**)



a: Z=H, b: Z=D, c: Z=CH_3, d: Z=Ph, e: Z=*p*-An

X=OTs, ONB

only.[3-5] The deuterated analogue (**1b**) produced **5b** and **7b** with the deuterium exclusively at C_2.[4,5] Interaction of the monoene and diene units of the cation, visualized by structures **2** and **3**, has been suggested to account for the observed path of rearrangement. The introduction of electron-releasing groups at C_9 (**1d,e**) did not affect the path of rearrangement.[6] However, in these cases not only the *cis-exo*-dihydroindenyl derivatives (**5d,e**) were formed, but also the cis-endo compounds (**6d,e**). The intermediacy of a bicycloaromatic ion **2** has also been proposed to explain the enhanced reactivity of *syn*-**1a** with respect to the more hydrogenated analogues.[5,6] Subsequently this interpretation was dismissed by Kirmse[7] on the basis of the observation that both *syn*- and *anti*-**1a** have identical rates and product mixtures. Therefore, the nature of the intermediate species remains unclear.[8]

In this paper we describe the results of a study on the ionization of the 9-methoxy derivative of **1** (**8**) and the more hydrogenated analogues (**9** and **10**) under conditions of short life, which proceeds without skeletal rearrangements. Furthermore, the 9-methoxybicyclo[4.2.1]nona-2,4-dien-9-yl cation (**21**) and the 11-methoxybicyclo[4.4.1]undeca-2,4,8-trien-11-yl cation (**25**) could be generated under conditions of long life. The NMR data reveal an unusual type of homoconjugation which is extensively discussed.

Results

Experiments under Conditions of Short Life. The α-chloro ethers **8**, **9**, and **10** were prepared by treatment of the corresponding dimethyl ketals with PCl_5 in ether. In contrast with the earlier reported 7-chloro-7-methoxynorbornene[9] which

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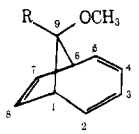
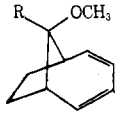
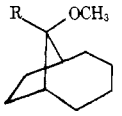
Table I. ^{1}H NMR Spectral Data[a] for Bicyclo[4.2.1]nonanes in $CDCl_3$ (δ)

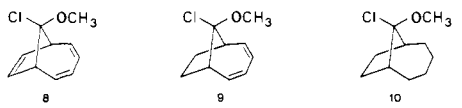
	R	$H_{1,6}$	H_{2-5}	$H_{7,8}$	OCH_3	others
	OCH_3	3.15 (m)	5.95 (m)	5.20 (d, J = 1.5)	3.12 (s) 3.22 (s)	
	Cl	3.55 (m)	5.97 (m)	5.40 (d, J = 1.5)	3.42 (s)	
	$C_6H_5N^+$	4.15 (m)	6.20 (m)	5.48 (d, J = 1.5)	3.12 (s)	9.60 (d, J = 7, H_o) 8.67 (m, H_p) 8.30 (m, H_m)
	OCH_3	2.60 (m)	5.72 (m)	2.05 (br m)	3.20 (s)	
	Cl	3.10 (m)	5.75 (m)	2.15 (m)	3.52 (s)	
	$C_6H_5N^+$	3.60 (m)	5.93 (m)	2.22 (m)	3.12 (s)	9.87 (d, J = 7, H_o) 8.78 (m, H_p) 8.32 (m, H_m)
	OCH_3	2.42 (m)	1.62 (m)	1.62 (m)	3.17 (s) 3.30 (s)	
	Cl	2.83 (m)	1.62 (m)	1.62 (m)	3.60 (s)	
	$C_6H_5N^+$	2.92 (m)	1.71 (m)	1.71 (m)	3.08 (s)	9.67 (d, J = 7, H_o) 8.46 (br m, $H_{m,p}$)

[a] J values are expressed in hertz.

Table II. Kinetic Data for the Reaction of Pyridine with Various 9-Chloro-9-methoxybicyclo[4.2.1]nonanes in CD_2Cl_2

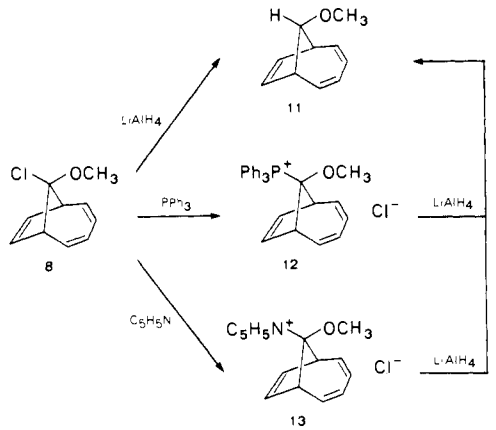
compd	temp, °C	10^4k[a], L mol^{-1} s^{-1}	rel k	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
8	31.0	14.98 ± 0.24		12.9 ± 0.4	−28.6 ± 1.3
	12.0	3.36 ± 0.08			
	−80.0 (ext)	2.5×10^{-5}	4.5×10^{-7}		
9	−30.6	14.54 ± 0.28		10.2 ± 0.5	−28.8 ± 1.9
	−44.2	3.90 ± 0.12			
	−80.0 (ext)	4.2×10^{-2}	7.6×10^{-4}		
10	−80.0	55.2 ± 1.0	1	7.2 ± 0.4	−30.6 ± 2.0
	−91.0	17.0 ± 0.7			

[a] Error in table indicates deviation from the average value of at least duplicate runs.



consisted of a mixture of epimers, one epimer was obtained for **8, 9,** and **10** only. Stereoselective reactions of the 9-bicyclo[4.2.1]nona-2,4,7-trienyl system have been encountered in the reduction of its ketone with agents such as phenyllithium, which afforded *syn*-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene only.[3] The stereochemistry was assigned on the basis of kinetic steric control, in which phenyllithium attacks the carbonyl group from the monoene side rather than across the butadiene bridge. Similarly the stereochemistry of structures **8, 9,** and **10** is inferred. Additional evidence is provided by their highly stereoselective reactions, which proceed without skeletal rearrangements.

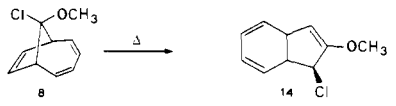
Scheme I



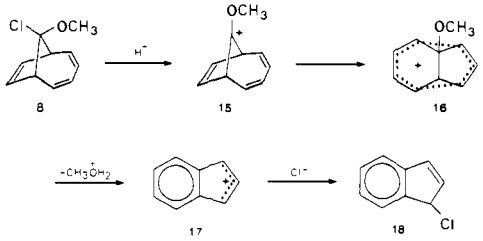
Reduction of **8** with lithium aluminum hydride produced the protic compound **11.** The stereochemistry of **11** can be assigned on the basis of its ^{1}H NMR spectrum. If H_9 is syn disposed with respect to the monoene bridge, its resonance signal exhibits a triplet (J = 6 Hz) due to coupling with the bridgehead protons, while this coupling is absent in the anti epimer.[3] Reaction of **8** with triphenylphosphine in liquid SO_2 at −40 °C provided the phosphonium salt **12.** Its configuration was established on the basis of the coupling of phosphorus with the bridgehead protons (J_{PH} = 14 Hz) and furthermore the shielding of the monoene protons (δ 4.97) and the deshielding of the butadiene protons (δ 6.23) with respect to corresponding absorptions of precursor **8** (Table I). Similar shielding effects of the triphenylphosphonium group were encountered in the norbornene series.[9] When **12** was reduced with lithium aluminum hydride, compound **11** was recovered. Thus, substitution proceeds with retention of configuration. A similar reaction pattern was observed for nucleophilic substitution with pyridine and subsequent reduction with lithium aluminum hydride (Scheme I). This stereoselectivity was established also for the more hydrogenated analogues **9** and **10.**

The progress of the reaction of compounds **8, 9,** and **10** with pyridine in methylene chloride was followed by integrating their ^{1}H NMR methoxy resonances (Table I) and those of the reaction products. Correct second-order plots were obtained in the range of 5-50% conversion. The rate constants together with the activation parameters are listed in Table II. The large negative values for the entropies of activation are in accord with a second-order process and similar to other Menschutkin reactions.[10]

Compound **8** appeared to be thermolabile. While no rearranged products were observed under solvolytic conditions, the indene derivative **14** was produced quantitatively on heating.[11]

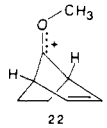


Experiments under Conditions of Long Life. Attempts to generate the 9-methoxybicyclo[4.2.1]nona-2,4,7-trien-9-yl cation (**15**) resulted exclusively in rearrangement and elimination. Thus, treatment of **8** in liquid SO_2 at −78 °C with FSO_3H produced 1-chloroindene (**18**) quantitatively. Presumably, the path of rearrangement included an initial 1,2 shift in cation **15**, which produced the 9-methoxyindenyl cation **16**. Subsequent elimination of methanol (**17**) and capturing of chloride afforded **18**.



The generation of the 9-methoxybicyclo[4.2.1]nona-2,4-dien-9-yl cation **21** was more successful. Its preparation was accomplished by dissolution of α-chloro ether **9** in a mixture of FSO_3H and liquid SO_2 at −60 °C. The structure of **21** was elucidated on the basis of its ^1H and ^{13}C NMR spectral data compared to those of the protonated ketone **20** and ketone **19**. From the NMR data and a computer simulation of the H_1-H_6 six-spin system the coupling constants and the chemical shifts of **20** and **21** were obtained. These parameters are collected in Figure 1 together with the ^1H NMR spectrum of **21**.

All carbon and proton resonances occur at different field. The asymmetry on either side of the ion may be due to the asymmetric dispositioning of the methoxy group in consequence of restricted rotation around the C-O bond.[12] However, this interpretation does not account for the spectral data. The C_2 resonance (δ 117.0) occurs upfield with respect to the signal for the comparable position C_5 (δ 123.5), whereas the resonance for the adjacent carbon C_3 occurs downfield (δ 133.6) as compared with that of C_4 (δ 124.2). The difference in the ^{13}C NMR resonances of the C_2-C_3 double bond ($\Delta\delta$ = 16.6) indicates considerable polarization of this bond. The value for the comparable C_4-C_5 bond ($\Delta\delta$ = 0.7) is insignificant. A further indication is obtained from the H_1-H_6 six-spin system, which shows a marked nonequivalence in the coupling constants $J_{1,2}$ (10.2 Hz) and $J_{5,6}$ (7.5 Hz). The value of $J_{1,2}$ = 10.2 Hz is close to that of the coupling constant between the adjacent olefinic protons, $J_{2,3}$ = 10.1 Hz. This indicates that the C_1-H_1 bond is coplanar with the plane of C_1, C_2, and C_3. On the contrary, the coupling constant $J_{5,6}$ = 7.5 Hz suggests a H_5-C-C-H_6 dihedral angle of about 25°.[13] Apparently, the carbon skeleton is distorted to an asymmetric structure. The steric requirement of an asymmetric dispositioned methyl group is insufficient to account for this effect as revealed by the ^1H NMR spectrum of the 7-methoxy-7-norbornenyl cation (**22**). This spectrum shows absorptions for the bridgehead



protons at different field, due to the shielding of the asymmetric positioned methyl group. However, no asymmetry in the H_1-H_4 four-spin system was observed. The olefinic resonances $H_{2,3}$ exhibit a triplet (J = 2.5 Hz) as a result of equivalent coupling constants on both sides of the ion.[12] Thus, the methyl group does not alter the dihedral angle between the bridgehead and olefinic protons.

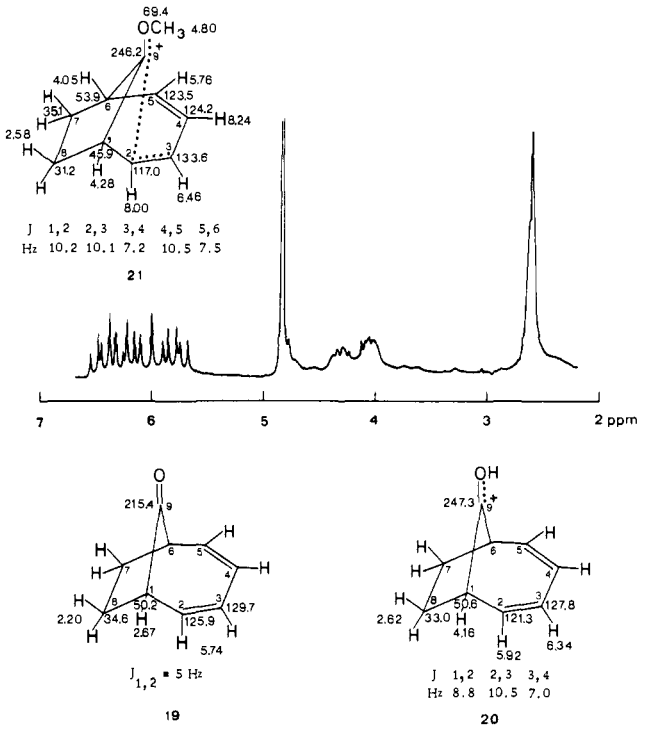
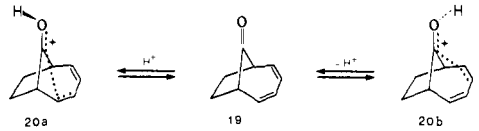


Figure 1. ^1H NMR spectrum of **21** and the ^1H and ^{13}C NMR spectral data (δ) for **20** and **21** in FSO_3H-SO_2 and **19** in SO_2 at −60 °C.

Additional evidence is provided by the NMR data of the protonated ketone **20** (Figure 1). The spectra reveal equivalent absorptions for both sides of the ion. This requires a fast exchange of the proton on oxygen with the solvent. The ^{13}C and ^1H NMR spectra of **20** show the equivalent absorptions amidst the corresponding nonequivalent absorptions of **21**. Moreover, the observed coupling constant $J_{1,2} = J_{5,6}$ = 8.8 Hz in **20** is the mean value of the dissimilar coupling constants $J_{1,2}$ = 10.2 and $J_{5,6}$ = 7.5 Hz in **21**. This indicates that the methyl group has little influence on these parameters.

All the available data are therefore consistent with an interaction of the cationic center with one of the double bonds of the butadiene system as implied in **21**. This interaction accounts for the induced polarization in one-half of the butadiene moiety. Furthermore, the increased coupling of one of the bridgehead protons (H_1) with the adjacent proton of the polarized double bond (H_2) indicates a bending of the C_1, C_9, C_6 bridge into the direction of this bond.[14] Obviously, in the protonated ketone **20** this interaction occurs alternately on either side of the ion owing to proton exchange on oxygen. As a consequence the time-averaged NMR spectrum of structures **20a** and **20b** is observed.



Interaction of a cationic center with a double bond should give rise to charge delocalization between these positions. Indeed, the downfield shift of C_9 in **20** and **21** relative to the carbonyl carbon in **19** ($\Delta\delta$ = 31.7 and 30.8, respectively) indicates less positive charge at the cationic center. The corresponding value for acetone and protonated acetone, in which no additional charge delocalization is present, comes to 45 ppm.[15]

In order to get more insight into the nature of the interaction of a cationic center with a butadiene system, the 11-methoxybicyclo[4.4.1]undeca-2,4,8-trien-11-yl cation (**25**) was studied.

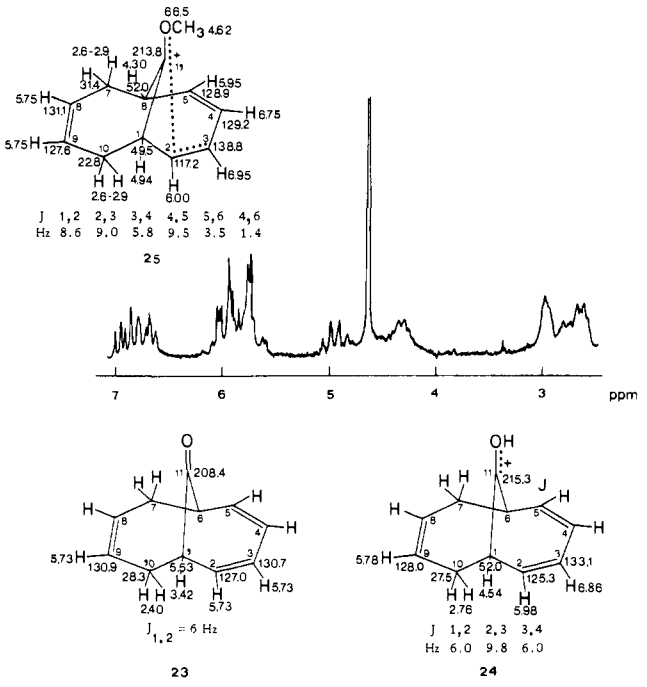


Figure 2. ^1H NMR spectrum of **25** and the ^1H and ^{13}C NMR spectral data (δ) for **24** and **25** in FSO_3H-SO_2 and **23** in SO_2 at −60 °C.

This system is more flexible with respect to structure **21,** consequent to the presence of the C_7–C_{10} four-carbon bridge. Therefore, in the case of an asymmetric interaction one would expect an enhanced skeletal distortion. This was confirmed by its NMR spectral data (Figure 2). The polarization in one-half of the butadiene moiety is increased as indicated by the difference in the ^{13}C NMR resonances for C_2 and C_3 ($\Delta\delta = 21.6$). Moreover, a larger difference in the coupling constants between the bridgehead proton and the adjacent olefinic proton on both sides of ion **25** was observed ($J_{1,2} = 8.6$ and $J_{5,6} = 3.5$ Hz). Finally, the downfield shift of the C_{11} carbon in **25** relative to the carbonyl resonance in ketone **23** ($\Delta\delta = 5.4$) indicates considerable electron delocalization to the cationic center. The downfield shift is even smaller than the corresponding value for protonated allylic ketones ($\Delta\delta \simeq 20$).[16]

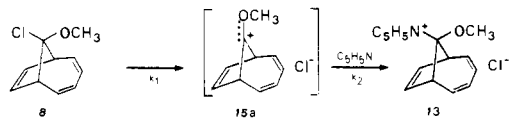
The NMR spectrum of protonated ketone **24** (Figure 2) shows equivalent resonances for both sides of the ion, similar to the protonated ketone **20,** with the averaged dissimilar values for comparable positions of ion **25.**

Quench experiments with **20, 21, 24,** and **25,** using a solution of sodium methoxide in methanol at −75 °C, afforded the corresponding ketals and ketones.

Discussion

The ionization reactions of 9-chloro-9-methoxybicyclo[4.2.1]nona-2,4,7-triene proceed without skeletal rearrangements. This result contrasts with earlier reports on the solvolysis of **1**-OTs and various 9-substituted derivatives (**1b–e**), which produced rearranged products only. Clearly, the major stabilization of the incipient cation by an α-substituted methoxy group prevents the rearrangement process. On the other hand, the residual positive charge at C_9 is sufficient to interact with the butadiene moiety as is revealed by the kinetic data of **8, 9,** and **10** and the NMR spectral data of ions **21** and **25.**[17]

Kinetics and Mechanism. The reaction of pyridine with compounds **8, 9,** and **10** proceeds with second-order kinetics and retention of configuration. This kinetic behavior can be rationalized on the basis of a rate-determining reaction of pyridine with the α-chloro ethers at the external ion-pair stage.[19] The intermediacy of a free carbonium ion is improbable since ionization of triene **8** under nonequilibrium conditions afforded solely rearranged products.



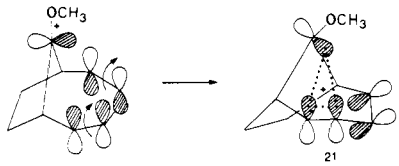
The stereospecific product formation observed for the completely saturated compound **10** evidently arises from steric factors which are prevailing in the bicyclo[4.2.1]nonane series.[3] In addition in diene **9** and triene **8** electronic factors may cooperate as indicated by the nonclassical structure of cation **21** under conditions of long life.

Stability and Bicycloaromaticity of the 9-Methoxybicyclo[4.2.1]nona-2,4,7-trien-9-yl Cation. Inspection of Table II shows the rate-retarding influence of the butadiene moiety in **9** with respect to the saturated analogue **10** ($k_9/k_{10} = 7.6 \times 10^{-4}$), whereas triene **8** is the least reactive in the series ($k_8/k_{10} = 4.5 \times 10^{-7}$). The rate depressions are too large to be accounted for by the inductive effects of the double bonds. They rather suggest that the intermediates involved are destabilized as a result of a homoconjugative 4π-electron interaction of the cationic center with the butadiene moiety. Strong support for this conclusion comes from the spectroscopic study of ions **21** and **25.** ^1H and ^{13}C NMR data point to an interaction of the cationic center with one of the double bonds of the butadiene system. The cations are distorted to an asymmetric structure which apparently is energetically more favorable than the symmetrical interaction which would be homoantiaromatic. However, the net result is a destabilized intermediate as is revealed by the rate retardation of **9** with respect to **10.** *This destabilization evidently arises from an overbalancing of the gain in resonance stabilization, as a result of the 2π-electron homoaromatic interaction in the ultimate asymmetric structure, by an increase in strain energy due to the concomitant skeletal distortion which occurs in order to attain a maximum interaction at one side of the ion.* Thus, the increase in $\Delta H^{\ddagger}$ of 3 kcal/mol from **10** to **9** is a consequence of increase in strain which is connected with an asymmetric structure in the transition state. This unfavorable energy path must be imposed by the homoantiaromatic symmetric situation. In this way the rate retardation of triene **8** with respect to diene **9** is consistent. The additional double bond in **8** makes the system more rigid. Consequently, the distortion of the carbon skeleton is more hampered. This is manifested in an increase in $\Delta H^{\ddagger}$ of 2.7 kcal/mol from **9** to **8.** Apparently, the additional double bond in **8** gives a minor contribution to the resonance stabilization of the system. This observation is in contrast with Goldstein's theory on topology and aromaticity,[2] which predicts cation **15** to be more stable than **21** as a consequence of longicyclic stabilization. Our results suggest that the [4.2.1] cation is destabilized because the homoantiaromatic interaction is the dominant factor. This conclusion is in better agreement with Goldstein's original definition,[1] which predicted the [4.2.1] cation to be destabilized on the basis of the dominance of the interaction of the odd bridge with the longer even bridge.

Orbital Symmetry Control over 4π-Electron Interactions. The asymmetric structure of ions **21** and **25** is most adequately elucidated on the basis of MO symmetry arguments. The π-atomic orbital of the one-carbon bridge will interact predominantly with the HOMO of butadiene. This molecular orbital is asymmetric with respect to the plane bisecting the bridgehead-bridgehead axis. Therefore, an asymmetric interaction can occur only (Figure 3). This interaction may be of the homoallylic type with one overlap (C_2-cationic center). Alternatively, two overlaps may be involved (C_2- and C_3-cationic center), which gives rise to a bishomocyclopropenyl

cation. Probably, the nature of ions **21** and **25** lies amidst both types. The interaction of C_3 is smaller than that of C_2 consequent to the differences in distance between these atoms and the cationic center. Moreover, this effect is increased as a result of the smaller coefficient of C_3 as compared with C_2 of the HOMO of butadiene. Thus, the structure of both ions can be represented as depicted in Figure 3.

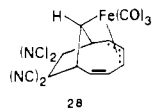
The molecular dynamics of the ionization process can be visualized by a conrotatory mode of motion. According to this description the absence of alternate interactions on either side of ions **21** and **25** is conceivable. On exchange of the asym-



21

metric interaction between the two double bonds, the ions should pass through a symmetric transition state. From symmetry reasons this has to occur via an electronic excited configuration of butadiene (LUMO). For the protonated ketones **20** and **24** alternation is possible as a result of proton exchange with the solvent, which gives rise to the intermediacy of the parent neutral ketones.

The occurrence of interactions with only a part of a conjugated system, here encountered in carbonium ions, finds its analogue in metal-coordination complexes.[20] A closely related example in this field (**28**) has been published recently by Paquette.[21]



28

Experimental Section

^{1}H NMR spectra were obtained on Varian Model T-60A and HA-100 spectrometers, equipped with variable temperature probes. Chemical shifts are reported relative to Me_4Si as internal standard.

^{13}C NMR spectra were obtained using a Varian Model HA-100 NMR spectrometer, equipped with FT accessory and variable temperature probe.

***anti*-9-Chloro-9-methoxybicyclo[4.2.1]nona-2,4,7-triene (8).** To a stirred solution of 9,9-dimethoxybicyclo[4.2.1]nona-2,4,7-triene[22] (5.2 g, 0.029 mol) in diethyl ether (5 mL) was added PCl_5 (6 g, 0.03 mol) in small portions at such a rate that the ether boiled gently. Sometimes addition of some phosphorus oxychloride was required to initiate the reaction. Because of its thermal lability, **8** was purified by high-vacuum evaporation of the solvent and volatile components ($POCl_3$ and CH_3Cl) for 1 h at 15 °C and subsequent recrystallization from pentane at −78 °C to give 3.2 g.

***anti*-9-Chloro-9-methoxybicyclo[4.2.1]nona-2,4-diene (9).** This compound was prepared from 9,9-dimethoxybicyclo[4.2.1]nona-2,4-diene[22] according to the previous procedure.

***anti*-9-Chloro-9-methoxybicyclo[4.2.1]nonane (10).** Boron trifluoride etherate (0.5 mL, 48%) was added to a solution of bicyclo[4.2.1]nonan-9-one[3] (1.0 g, 7.5 mmol) in methanol (25 mL) at 0 °C. The mixture was allowed to stand overnight in a refrigerator. After neutralization with saturated sodium bicarbonate at 0 °C, the solution was extracted with ether. The ether layer was washed with saturated sodium chloride, dried ($MgSO_4$) and concentrated. The product was purified by chromatography on a silica gel column, eluting with ether–hexane mixtures to give 9,9-dimethoxybicyclo[4.2.1]nonane. The dimethyl ketal was converted to α-chloro ether **10** according to the procedure described above.

11-Chloro-11-methoxybicyclo[4.4.1]undeca-2,4,8-triene. This compound was prepared from bicyclo[4.4.1]undeca-2,4,8-trien-11-one[23] according to the previous procedure: δ_{Me_4Si} ($CDCl_3$) 5.84 (m, 6 H), 3.58 (s, 3 H), 3.30 (m, 2 H), and 2.54 (m, 4 H).

***cis-exo*-2-Methoxydihydroindenyl Chloride (14).** Vacuum distillation of triene **8** provided **14**: ^{1}H NMR δ_{Me_4Si} ($CDCl_3$) 5.73 (m, 4 H), 4.69 (m, 2 H), 3.71 (s, 3 H), and 3.50 (m, 2 H); ^{13}C NMR δ_{Me_4Si}

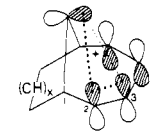


Figure 3.

($CDCl_3$) 160.1 (s), 128.4 (d), 126.6 (d), 123.8 (d), 121.9 (d), 100.9 (d), 69.2 (d), 58.5 (q), 47.1 (d), 39.3 (d).

Reaction of 8 with Lithium Aluminum Hydride. To a stirred solution of **8** (1 g, 5.5 mmol) in dry diethyl ether (10 mL) was added lithium aluminum hydride (0.5 g, 13 mmol) in 15 min. The excess hydride was hydrolyzed with 3 N sodium hydroxide and the ether was washed with water and evaporated. The residue was distilled to give **11** (0.45 g), by 34–36 °C (0.1 mm): δ_{Me_4Si} ($CDCl_3$) 5.93 (m, 4 H), 5.13 (d, J = 1.5 Hz, 2 H), 3.80 (t, J = 6 Hz, 1 H), and 3.10 (m, 5 H).

***anti*-9-Methoxy-9-bicyclo[4.2.1]nona-2,4,7-trienyltriphenylphosphonium Fluoroborate (12).** To a solution of **8** (1 g, 5.5 mmol) in liquid sulfur dioxide (10 mL) was added triphenylphosphine (1.5 g, 5.7 mmol). After 15 min of stirring at −50 °C, trimethyloxonium fluoroborate (0.8 g, 5.5 mmol) was added. The reaction mixture was stirred for an additional 15 min and poured into dry ethyl ether, whereupon **12** (2.2 g) preciptated as white crystals: mp 230–234 °C dec; δ_{Me_4Si} (SO_2) 7.82 (m, 15 H), 6.23 (m, 4 H), 4.97 (d, J = 1.5 Hz, 2 H), 4.13 (d, J = 14 Hz, 2 H), and 2.87 (d, J = 1.5 Hz, 3 H).

***anti*-9-Methoxy-9-bicyclo[4.2.1]nona-2,4,7-trienylpyridinium Fluoroborate (13).** This compound was prepared from **8** and pyridine as described in the previous experiment.

Reaction of 12 with Lithium Aluminum Hydride. To a suspension of **12** (2 g, 3.6 mmol) in dry tetrahydrofuran at −78 °C was added lithium aluminum hydride (0.1 g, 2.6 mmol). The mixture was stirred for 1 h and was then allowed to warm to room temperature. The excess hydride was hydrolyzed with 3 N sodium hydroxide and the aqueous layer was extracted with ether. The ether extracts were washed with water, dried, and concentrated. Vacuum distillation provided pure **11** (0.42 g).

Kinetic Measurements. Equimolar amounts of pyridine and α-chloro ether dissolved in CD_2Cl_2 were mixed at −80 °C for compounds **8** and **9** and at −140 °C for **10** in an NMR sample tube (0.4–1.0 M solution). The runs were performed at temperatures as indicated in Table II. The progress of the reaction was followed by integrating the ^{1}H NMR methoxy signals of substrate and product at appropriate intervals. The rate constants were determined graphically.

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Oxasecoalkylation via Cyclobutanone Intermediates

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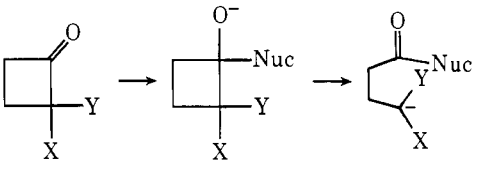
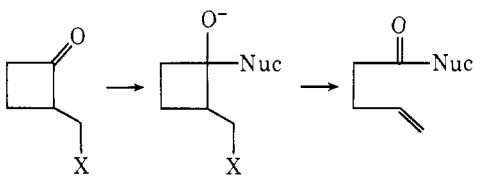
Abstract: [*n*,4]Spiroannelation of α,β-epoxy ketones utilizing diphenylsulfonium cyclopropylides followed by fragmentation constitutes a novel chain extension procedure. The fragmentation has been shown to be stereospecificially anti. From one diastereomer of an epoxycyclobutanone, fragmentation can produce either olefin geometry in the chain-extended product. Conversion of the cyclobutanone to a cyclobutanol prior to fragmentation also allows facile subsequent cleavage to a ketone. An annelation that complements the Robinson "annelation" has been developed based upon this sequence. Utilizing the methyl-substituted ylide and an epoxyperhydroindanone, model studies directed toward steroids have been explored. The sequence is a synthetic equivalent of a carbanion β to a carbonyl group concomitant with regio- and stereocontrolled introduction of a γ,δ double bond.

The potential of small-ring chemistry in organic synthesis depends upon controlled molecular reorganization in the release of the strain energy. One such approach is embodied in the nucleophilically triggered cleavage of cyclobutanones (eq 1).[1,2] Such reactions require the presence of some group(s) at



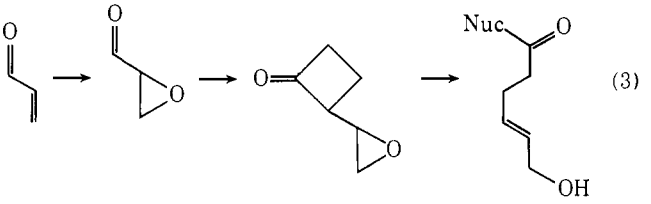
(1)

the α carbon in order to stabilize the incipient carbanion. Previously X and/or Y as halogen,[1a,c,f,h,2e,h] alkyl- or arylthio substituents,[1b,e,g,2i] olefins,[2a-d,g] aromatic rings,[1f,2f] or acyl groups[1d] have proven successful. An alternative envisions placing a potential leaving group β to an incipient carbanion in order to induce a fragmentation (eq 2). Fragmentation re-



(2)

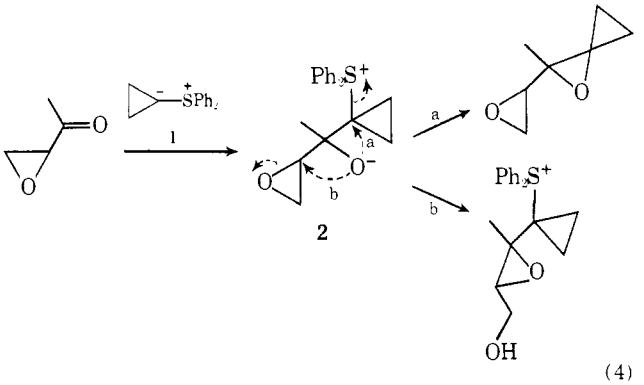
actions have played a major role in organic chemistry.[3] Interest in the above sequence stems from the facility of forming the requisite system by [*n*,4]spiroannelation of carbonyl compounds.[4] A particularly intriguing aspect of this sequence is the ability to elaborate enones via their corresponding α,β-epoxycarbonyl systems as summarized in eq 3. The introduction of cyclic units by initial ring formation followed by ring cleavage has been termed secoalkylation. In this case, since one of the ring atoms is oxygen, it is termed oxasecoalkylation. In



(3)

this paper we wish to report the realization of this approach and the determination of its stereochemistry.[5]

Two major problems concerned us. The first problem was the possibility of a competition in the elimination step of the cyclobutanone annelation utilizing the sulfur ylide **1**. Thus, the



(4)

intermediate **2** could effect epoxide ring opening (path b, eq 4) in competition with the desired sulfide displacement (path a, eq 4). The latter process, an S_N2 displacement at a cyclopropyl carbon, normally is anticipated to be a relatively high activation energy process. The fact that it occurs under such mild conditions with **1** and simple carbonyl partners remains a delightful mystery[6] that is compounded by the fact that the corresponding sulfoxamine ylide does not possess a similar

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