The Importance of Nonbonded Interactions in the Bicyclo[4.2.1]nona-2,4,7-trienyl System[1]

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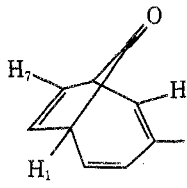
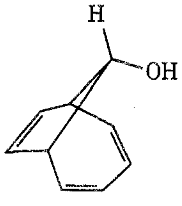
Spectral evidence is presented showing the importance of nonbonded interactions in the 9-bicyclo[4.2.1]nonatrienyl system when charge is induced at C_9. CNDO/2 calculations were made for the corresponding cation in a variety of geometries. The geometric variations were designed such that they are in line with the rearrangement process observed in the reactions of these compounds. The implications of the combined results from the spectral measurements and the calculations on the solvolytic reactions of these compounds are significant and in general emphasize the strong involvement of the four-carbon bridge containing the butadiene moiety.

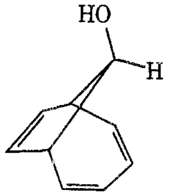
Recent work by Schweig shows the importance of through-space interactions between adjacent chromophores in the bicyclo[4.2.1]nona-2,4,7-trienyl system.[2] The photoelectron spectra of bicyclo[4.2.1]nona-2,4,7-trienone (I) shows that the compound is not bicycloconjugated[3] but instead is homoconjugated where the *n* molecular orbital of the ketone group interacts directly with the butadiene moiety. These results have a bearing on the nature of the cation formed in solvolyses of *endo*-II-OTs[4] and *exo*-II-OTs,[5,6] protonation of 9-*exo*-methylenebicyclo[4.2.1]nona-2,4,7-triene,[7] and photolysis of bicyclo[4.2.1]nona-2,4,7-trien-9-one tosylhydrazone in CH_3OH-CH_3ONa,[5] or by the ionization of *endo*-II-OSOCl.[8] In order to gain a further understanding of the delocalization which occurs when charge is induced at or near the 9 carbon of these bicyclic structures, we approached the problem using spectroscopic measurements and CNDO/2 calculations.



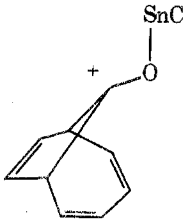
I



endo-II-OH



exo-II-OH



III

Spectroscopic Measurements. NMR measurements were made on the ketone I under a variety of conditions in order to determine the effect of positive charge formally introduced into the carbonyl carbon. Table I lists chemical shifts for the various hydrogens in I as measured on a Varian HR220. Assignment of the signals is based on the coupling constants, which do not vary greatly with the changes in conditions. The coupling constants (hertz), $J_{1,2}$ and $J_{1,8}$, are 7.5 and 1 in CCl_4, and are ~7 and 1.4 in SO_2, respectively. These values vary by ca. 0.1 Hz with the addition of metal salts to the sample solutions.

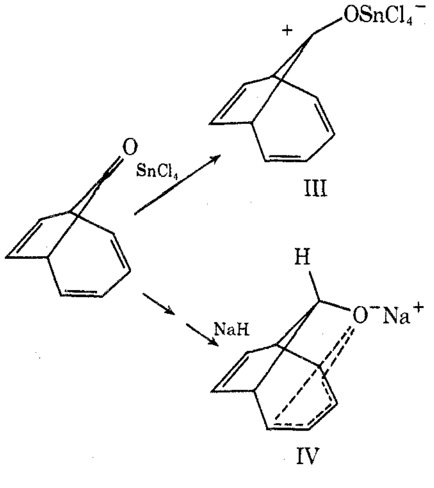
The spectra of I in CCl_4 containing 2 equiv of $Eu(fod)_3$ show all the signals deshielded where the bridgehead hydrogens feel the greatest effect. The effect on all the olefinic hydrogens is approximately comparable and considerably less than on the bridgehead hydrogens. The signal for $H_{2(5)}$ is shifted more than the signal for $H_{3(4)}$ which in turn is shifted only slightly more than that for $H_{7(8)}$.

The addition of 4 equiv of $SnCl_4$ to a solution of I in liquid SO_2 at −40° produces a burgundy-colored solution owing to complex formation (III). The ketone is recovered in good yield on quenching of this solution in methanol containing K_2CO_3. The recovered material contained 5% of another product whose structure was not identified. The NMR spectra of the ketone–$SnCl_4$ complex shows all the signals deshielded as a result of the induced positive charge, and the shifts are similar to those previously observed for other ketone–$SnCl_4$ complexes.[9]

The bridgehead hydrogens again experience the largest shift. The monoene hydrogens show little effect, while the butadiene hydrogens are shifted more significantly. Clearly very little charge is delocalized into the olefinic region, but to the extent that it occurs, it involves the butadiene π system primarily. Thus, polarization of the carbonyl group by a Lewis acid enhances homoconjugation between the carbonyl group and the butadiene π system.

Homoconjugation still prevails in the salts (IV) (Scheme I) of the endo carbinol II-OH, formed by reduction of I. The addition of 2 equiv of NaH to *endo*-II-OH in DME produces a bright red solution. The visible spectrum of the solution shows a broad band with λ_{max} at 538 nm and ϵ equal to 114. However, the NMR spectra of a 1 *M* solution of this alkoxide revealed that none of the olefinic protons

Scheme I



had shifted relative to those for *endo*-II-OH. The carbinol is recovered quantitatively on quenching with water. In contrast, no color was observed on treatment of a 1 *M* solution of *exo*-II-OH in DME with NaH. Thus, delocalization of the charge on the alkoxide oxygen into the π system in IV occurs preferentially through the butadiene moiety.

The experimental results indicate that homoconjugation between the one-carbon bridge and the butadiene moiety is important with little or no involvement of the other double bond. This is the case when the compound is neutral,[2] when the carbonyl has an induced positive charge, and when the oxygen of the reduced carbinol is negatively charged. While the noninvolvement of the simple double bond may be due to electronic considerations, it might also be attributed to its remoteness and its orientation as a result of the near-planar arrangement of the five-membered ring.

CNDO/2 Calculations. The electronic structure of the 9-bicyclo[4.2.1]nona-2,4,7-trienyl cation was analyzed using the CNDO/2 method.[10,11] The program contained the BINDEX subroutine for calculating bond indices as previously described by Wiberg.[12] The initial geometric parameters were measured directly from a model constructed with Drieding models and submitted to the GEOM subroutine which calculated the Cartesian coordinates. The calculations of the energy, electron density, and bond indices (Table II) were then based on this conformation and its corresponding coordinates (Figure 1).

In the initial calculations for the cation, the C_2 to C_8 distance was maintained at 2.47 Å and the C_9 bridge was tipped relative to the other two bridges. There is always a small residual bond index between C_2 and C_5 (0.09). In the undistorted cation the C_2–C_1–C_9 bond angle is 109.30°. First, aside from the olefinic sites, the C_1–C_2 bond is significantly delocalized resulting in a corresponding increase in bond indices between $C_1(C_6)$–C_9 and $C_2(C_5)$–C_9. The interactions between $C_2(C_5)$–$C_8(C_7)$ and $C_8(C_7)$–C_9 are only slight. Movement of the one-carbon bridge toward the two-carbon bridge reduces the degree of delocalization and destabilizes the system. Movement toward the butadiene moiety stabilizes the system in a smooth way to a minimum value when the C_2–C_1–C_9 bond angle is 100.00°. The total stabilization gained by this 10° change is 7.2 kcal.

This stabilization is accompanied by a further weakening of the $C_1(C_6)$–$C_2(C_5)$ bond and an increase in the $C_2(C_5)$–C_9 interaction. The charges at most of the atoms are hardly affected by this change and are equal to C_1 (+0.024), C_2 (+0.036), and C_3 (+0.008). The observed changes are from +0.002 to −0.001 at $C_8(C_7)$ and from +0.307 to +0.282 at C_9 when the bond angle decreases from 110° to 100.0°, respectively.

The description of the cation which emerges from these calculations indicates that the charge at C_9 is slightly dispersed into carbons $C_1(C_6)$ and $C_2(C_5)$ primarily. This results from the delocalization of the σ bonds $C_1(C_6)$–$C_2(C_5)$, and occurs with little change in the electronic character of the monoene and butadiene moieties. Structure VI (Scheme II) shows these interactions.

One other variation was attempted in order to further define the nature of the cation. Guided by the molecular rearrangements observed under solvolytic conditions,[4,6] the tipped cation VI was further distorted in order to reduce the interatomic distance between $C_2(C_5)$ and $C_8(C_7)$. This was accomplished by rotating the cyclopentenyl substructure (C_1, C_9, C_6, C_7, C_8) about an axis defined by the bridgehead carbons. The general symmetry of the molecule is maintained where the only changes are the decrease in the bond angle C_8–C_1–C_2 and the corresponding increase in the bond angle C_9–C_1–C_2.

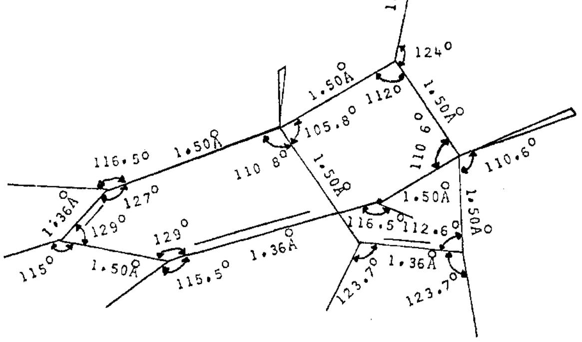


Figure 1.

Table I
Chemical Shifts of Bicyclo[4.2.1]nona-2,4,7-trien-9-one at 220 MHz

H	Chemical shifts, Hz from Me_4Si		$\Delta\delta$	
	CCl_4[a]	CCl_4 with $Eu(fod)_3$[a]	Hz	δ
1(6)	655	1068	413	1.88
2(5)	1270	1419	149	0.68
3(4)	1270	1402	132	0.60
7(8)	1258	1382	124	0.56
H	SO_2[b]	SO_2 with $SnCl_4$[b]	Hz	δ
1(6)	703	831	128	0.58
2(5)	1292	1303	11	0.05
3(4)	1292	1328	25	0.11
7(8)	1269	1273	4	0.02

[a] 25°. [b] −40°.

Table II
Results of Calculations of the Bicyclo[4.2.1]nona-2,4,7-trienyl Cation

Bond angle for C_2–C_1–C_9	Energy, kcal	Bond indices									Interatomic distances	
		C_1–C_2	C_1–C_9	C_1–C_8	C_2–C_3	C_3–C_4	C_2–C_9	C_2–C_8	C_8–C_9	C_8–C_7	C_2–C_9	C_8–C_9
120.0	−44,148.5	0.95	1.07	0.94	1.88	1.09	0.05	0.02	0.07	1.88	2.62	2.21
109.3	−44,173.3	0.90	1.11	0.97	1.88	1.09	0.09	0.02	0.03	1.89	2.44	2.26
106.9	−44,176.5	0.89	1.11	0.98	1.88	1.09	0.09	0.02	0.03	1.89	2.40	2.28
106.0	−44,177.6	0.89	1.11	0.98	1.88	1.09	0.10	0.02	0.03	1.89	2.39	2.28
103.5	−44,179.8	0.88	1.11	0.99	1.88	1.08	0.11	0.02	0.03	1.89	2.35	2.30
102.0	−44,180.8	0.88	1.11	0.99	1.88	1.08	0.11	0.02	0.02	1.89	2.33	2.31
100.0	−44,181.5	0.88	1.10	1.00	1.87	1.08	0.11	0.02	0.02	1.88	2.30	2.33
98.0	−44,181.3	0.88	1.10	1.00	1.87	1.08	0.12	0.02	0.02	1.88	2.27	2.35

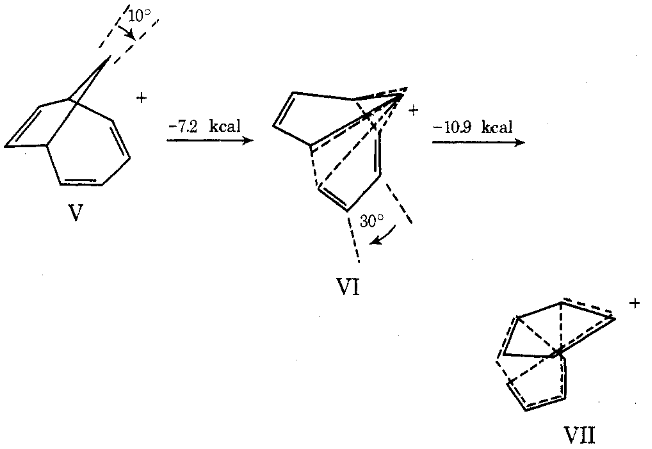
Table III
Calculations on Cation VI

Bond angle $C_2-C_1-C_8$	Energy, kcal	Bond indices								
		C_1-C_2	C_1-C_9	C_1-C_8	C_2-C_3	C_3-C_4	C_2-C_9	C_2-C_8	C_8-C_9	C_7-C_8
110.6	−44,181.5	0.88	1.10	1.00	1.87	1.08	0.11	0.02	0.02	1.88
107.1	−44,182.7	0.88	1.11	0.99	1.87	1.09	0.11	0.03	0.03	1.87
104.6	−44,183.3	0.87	1.12	0.98	1.86	1.09	0.10	0.04	0.03	1.86
103.7	−44,184.1	0.87	1.13	0.98	1.86	1.10	0.10	0.05	0.03	1.86
101.3	−44,183.8	0.87	1.13	0.97	1.85	1.10	0.10	0.06	0.03	1.84
95.6	−44,183.9	0.86	1.15	0.95	1.83	1.12	0.08	0.10	0.04	1.80
90.6	−44,187.1	0.85	1.17	0.93	1.79	1.14	0.08	0.15	0.05	1.74
86.6	−44,189.1	0.84	1.19	0.91	1.76	1.15	0.07	0.20	0.06	1.67
85.6	−44,189.9	0.84	1.20	0.91	1.75	1.16	0.07	0.21	0.06	1.65
84.6	−44,190.5	0.83	1.20	0.90	1.74	1.16	0.06	0.22	0.06	1.64
82.6	−44,191.6	0.83	1.21	0.89	1.71	1.17	0.06	0.26	0.07	1.59
80.6	−44,192.4	0.82	1.22	0.88	1.69	1.17	0.05	0.29	0.07	1.55
78.6	−44,187.5	0.81	1.23	0.86	1.67	1.18	0.05	0.33	0.08	1.51
75.6	−44,186.2	0.80	1.23	0.85	1.64	1.18	0.04	0.38	0.08	1.43
67.4	−44,175.4	0.80	1.05	0.93	1.62	1.04	0.01	0.46	0.09	1.09

Table IV
Calculations on Cation VI

Bond angle $C_2-C_1-C_8$	Charge densities					Interatomic distance C_2-C_8, Å
	$C_1(C_6)$	$C_2(C_5)$	$C_3(C_4)$	$C_7(C_8)$	C_9	
110.6	3.976	3.964	3.992	4.001	3.718	2.47
107.1	3.976	3.959	3.995	4.000	3.718	2.41
104.6	3.976	3.995	3.997	3.999	3.720	2.37
103.7	3.977	3.953	3.998	3.998	3.721	2.36
101.3	3.977	3.949	4.000	3.997	3.725	2.32
95.6	3.979	3.937	4.004	3.992	3.740	2.22
90.6	3.983	3.923	4.008	3.987	3.757	2.13
86.6	3.985	3.911	4.010	3.984	3.779	2.06
85.6	3.985	3.908	4.010	3.983	3.785	2.04
84.6	3.986	3.905	4.010	3.981	3.792	2.02
82.6	3.985	3.898	4.008	3.980	3.809	1.98
80.6	3.987	3.892	4.007	3.976	3.826	1.94
78.6	3.989	3.886	4.005	3.974	3.840	1.90
75.6	3.987	3.878	3.999	3.959	3.884	1.84
67.4	3.960	3.905	3.912	3.874	4.202	1.66

Scheme II



As can be seen by the results listed in Table III, this motion further stabilizes the system in a smooth way to a minimum value when the $C_8-C_1-C_2$ bond angle is 80.6° and the $C_2-C_1-C_9$ bond angle is 130.0°. That is, closing the angle 30° stabilizes the cation by 10.9 kcal. The resulting structure has minimal through-space interactions of the olefinic moieties with the cation center at C_9. On the other hand, the closer proximity of $C_2(C_5)$ and $C_8(C_7)$, 1.94 Å, increases the interaction between the monoene and diene where the final bond index is 0.29. The bond indices for the monoene and butadiene moieties are significantly reduced, but the π character of the butadiene structure is preserved with the central bond (C_3-C_4) maintaining a lower bond index.

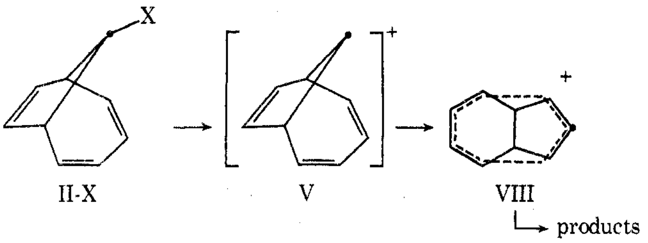
The other changes occur in the formal σ structure, where $\sigma_{1,2}$ and $\sigma_{6,5}$ are further delocalized, the bonds $\sigma_{1,8}$ and $\sigma_{6,7}$ are also delocalized and the double bond character between $C_1(C_6)$ and C_9 increases. Accompanying these electronic changes is a shift of the partial positive charge from $C_1(C_6)$ and C_9 to $C_2(C_5)$ (Table IV). The centers $C_3(C_4)$ and $C_7(C_8)$ continue to feel very little charge.

One final operation which was performed, but the results are not tabulated, involved elongation of the $C_1(C_6)-C_2(C_5)$ bonds at various points down Table III. The effect of bond elongation was to destabilize the system in every case.[13]

Discussion

Treatment of ketone I with $SnCl_4$ in liquid SO_2 at low temperatures successfully induced sufficient charge at C_9 to permit observation of the shifts of the hydrogen signals in the NMR spectra, but not enough to permit the rear-

Scheme III



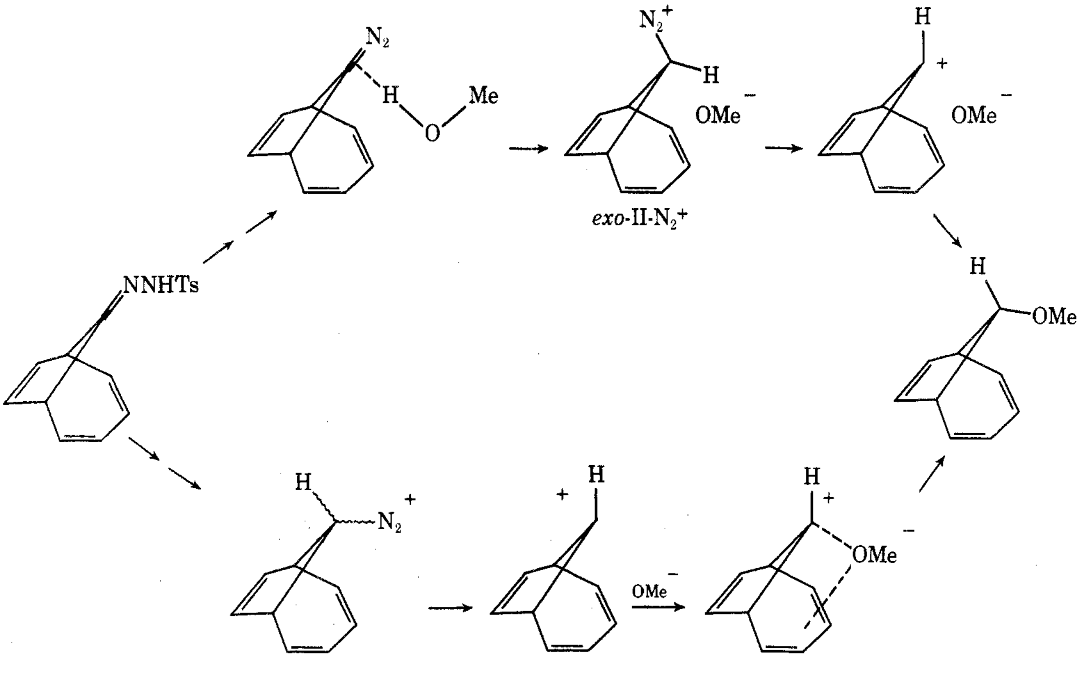
rangement process to occur (Scheme III). Delocalization of charge away from C_9 into the olefinic moieties is probably minimal, since it is a tertiary center with an oxygen substituent. However, some charge is delocalized and primarily into the butadiene. In line with these observations, calculations on the unsubsituted cation (V) reveal that C_9 interacts to a slight extent with the butadiene moiety, and that the cation is substantially stabilized by slight tipping of C_9 toward the four-carbon bridge.

Regarding the character of the "tipped" cation (VI), it is not simply a 1,2-bishomocyclopentadienyl cation, which is antihomoaromatic, since there is a significant delocalization of the C_1–C_2 and C_6–C_5 σ bonds plus an accompanying increased interaction between C_2 and C_5. Furthermore, some level of interaction, although slight, is always maintained with the monoene.

The unrearranged cation (V) (Scheme IV) described here has some interesting implications on the solvolytic behavior of *endo*-II-OTs[4] and *exo*-II-OTs.[5,6] First of all, the rearrangement of cation V to form VIII competes very efficiently with chemical capture. However, to the extent that V can be captured, both steric and electronic considerations would predict chemical capture at C_9 to form exo product.

Contrary to this expectation, chemical capture of the cation produced in the photolysis of bicyclo[4.2.1]nona-2,4,7-trien-9-one tosylhydrazone in methanol is reported to yield only *endo*-II-OMe plus the rearranged products and no *exo*-II product.[5] Thus, in this reaction either the protonation step to produce *exo*-II-N_2^+ is stereospecific where the approach of the methanol is endo, generating a tight ion pair[14,15] which subsequently produces *endo*-II-OMe, or there is no specificity in the steps leading to the generation of cation V but the approach of the methoxide anion is guided endo by the stabilizing interaction with the butadiene moiety or a combination of these effects. The latter view is supported by the observed interaction between the negative oxygen atom and the butadiene moiety in IV.

Scheme IV

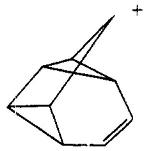


In line with this view, the ionization of *endo*-II-OTs may proceed with considerable interaction between the forming toluenesulfonate anion and the butadiene moiety. With this interaction present, the solvolytic rates of *endo*-II-OTs will have a relatively low solvent sensitivity.[6]

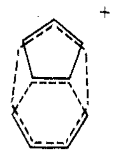
The stability of cation V was calculated for a variety of conformations produced by tipping the one-carbon and the four-carbon bridge. Tipping of the one-carbon bridge toward the four-carbon bridge and subsequent tipping of the four bridge toward the two-carbon bridge produces a smooth exothermic change which results in a cation which is further stabilized by as much as 18 kcal.

While we do not pretend to know the exact mechanism for the ionic rearrangement reaction which results in the formation of the bishomotropylium ion (Scheme III), the simple operations performed here on cation V prove to be energetically very favorable and could possibly resemble the initial stages of the rearrangement reaction. It is realized that the geometries used in these calculations are at best good approximations of the real system, since neither vibrations of the cationic system away from the equilibrium geometry nor solvation were taken into account. However, the implications of this work are that the initial stages of the rearrangement reaction must proceed via an efficient exothermic pathway with no significant minimums. Secondly, regarding the character of the cation when $C_2(C_5)$ migrates from $C_1(C_6)$ to $C_8(C_7)$, the results in Table III show that the process which continues to close the distance between $C_2(C_5)$ and $C_8(C_7)$ with a possible resultant formation of a biscyclopropylcarbinyl cation, X, is energetically very costly. That is, reduction of this distance to 1.66 Å destabilizes the cation by 17 kcal.

It may well be that all pathways leading from VII to VIII will include some endothermic steps, where those involving structures like IX will prove less favorable because of the steric strain considerations than those involving more delocalized structures like X.



IX



X

Experimental Section

***exo*-Bicyclo[4.2.1]nona-2,4,7-trien-9-ol.** A solution containing 10 g of ketone I,[4] 50 g of aluminum isopropoxide, freshly distilled (131–134°, 4–5 mm), 0.5 ml of acetone, and 500 ml of xylene, dried over sodium, was refluxed for 12 hr. To the cooled mass was added 100 ml of 10% aqueous NaOH and the mixture was extracted with ether. After the ethereal extract was washed with water and dried, the ether and xylene were removed by distillation at 1 atm. The remaining residue was chromatographed on 100 g of activity III alumina. The pentane fractions contained 6.17 g of *endo*-II-OH while the 50% ether–pentane fractions contained 1.66 g of *exo*-II-OH.

Analysis of the ethereal extract before distillation by VPC on a 2-m column containing 2.5% KOH–Carbowax 20M on Chromosorb W 80/100 mesh at 120° revealed a mixture of 80% *endo*-II-OH (4.5 min) and 20% *exo*-II-OH (11.0 min). Only 0.1% of another product was detected. This endo/exo ROH ratio of 4:1 did not change when the reaction mixture was heated for up to 4 days.[5]

Epimerization of *exo*-II-OH under the same conditions for 16 hr gave a 1:4 endo/exo ROH mixture.

The carbinol, *exo*-II-OH, was recrystallized from hexanes: mp 84–85°; ir (KBr) 3250, 3160, 3140, 2960, 2920, 1580 cm^{-1}; δ_{Me_4Si} (CS_2) 5.84 (m, 2.04, H_2), 5.69 (m, 2.04, H_3), 5.13 (d, J = 1.5 Hz, 2.04, H_7), 3.77 (s, 0.95, H_9), 2.78 (d, J = 7.2 Hz, 2.00, H_1), and ca. 2.8 (broad, 0.94, OH). The exo stereochemistry is indicated by the lack of coupling between H_1 and H_9.

Preparation of Ketone–$SnCl_4$ Complex. Sulfur dioxide (0.4 ml) was distilled into a NMR tube containing 34 mg of ketone I under nitrogen at −78°. Excess $SnCl_4$, 2–5 equiv, was added and the tube was stoppered. Spectral measurements were made at −40°.

After 0.5 hr, 1 ml of saturated Na_2CO_3 in methanol was added and the mixture was extracted with ether in the usual manner. The ketone I was recovered in 25% yield, and was >95% pure. Long reaction times produced ca. 10% of another ketonic product, not identified ($\nu_{C=O}$ 1720 cm^{-1}).

While the recovery from liquid SO_2 was poor (25%), the recovery from a nitromethane solution was good. The ketone was recovered in 93% yield along with 5% of an aromatic product.

Preparation of Sodium Alcoholates. To 1 mmol of the carbinol in 1 ml of anhydrous DME was added 2 equiv of pentane-washed sodium hydride with stirring. Color developed after a few minutes with the *endo*-II-OH. After NMR measurements were made at 0°, the solutions were diluted with DME and the uv–visible spectra were measured. *endo*-II-OH had λ_{max} 538 nm (ϵ 114) while *exo*-II-OH had no spectra. The solutions were quenched with wet ether and worked up in the usual way. The recovered yield of *endo*-II-OH was 91%.

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Registry No.—I, 34733-74-9; *endo*-II-OH, 34712-67-9; *exo*-II-OH, 55606-59-2; III, 55606-56-9; *endo*-IV, 55606-60-5; *exo*-IV, 55606-61-6; 9-bicyclo[4.2.1]nona-2,4,7-trienyl cation, 50613-69-9; aluminum isopropoxide, 555-31-7; $SnCl_4$, 7646-78-8; sodium hydride, 7646-69-7.

References and Notes

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Synthesis and Chemistry of 2,4-Dehydro-5-homoadamantanone[1]

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2,4-Dehydro-5-homoadamantanone (**5**) is readily prepared by a four-step reaction sequence from bicyclo[3.3.1]non-6-ene-3-carboxylic acid. Treatment of **5** with lithium in liquid ammonia proceeds by regiospecific cleavage of the C-3 to C-4 bond in **5** to give tricyclo[5.3.1.0^{4,9}]undecan-2-one (**27**). In contrast, perchloric acid catalyzed acetolysis of **5** leads to regiospecific cleavage of the C-2 to C-4 bond in **5** and formation of 2-*exo*-acetoxy-5-homoadamantanone. Sodium borohydride reduction of **5** occurs stereospecifically to afford 2,4-dehydro-5-*endo*-homoadamantanol (**9**). Acid-catalyzed isomerization of **9** provides 2-*exo*-homoadamant-4-enol exclusively which, in turn, gives homoadamant-4-en-2-one (**14**) upon Jones oxidation. Sodium borohydride reductions of enone **14** and ketone **27** both proceed by stereospecific attack at the exo face of the carbonyl carbon. The stereospecific synthesis of both 2-exo- and 2-endo-substituted homoadamantanes is presented. It is also shown that the stereochemistry of a 2-monosubstituted homoadamantane can be directly assigned from its characteristic ^{1}H NMR spectrum.

Homologation of 8,9-dehydro-2-adamantanone (**1**), without disruption of the conjugated cyclopropyl ketone moiety, allows for four "dehydrohomoadamantanones", **2–5** (Scheme I). As **1** has been shown to be a useful precursor for the synthesis of adamantyl,[3-6] protoadamantyl,[5-8] and isotwistyl[8,9] derivatives, cyclopropyl ketones **2–5** offer the potential for the synthesis of a variety of variously substituted polycyclic compounds. Recently, we have prepared