Arylallyl cations and their stereospecific cyclization to bicyclic trienylic cations

D. M. DYTNERSKI, K. RANGANAYAKULU, B. P. SINGH, AND T. S. SORENSEN
The Department of Chemistry, University of Calgary, Calgary, Alta., Canada T2N 1N4

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A series of arylallyl alcohols, where aryl = 2,6-dimethylphenyl, mesityl, duryl, or pentamethylphenyl, was prepared. On addition to strong acid, these generate arylallyl cations. In some cases these allyl cations are observable and were characterized as *in situ* solution species by nmr spectroscopy. In other cases, an immediate cyclization takes place, leading stereospecifically to a series of bicyclic trienyl cations, which were also thoroughly characterized. The stereochemistry of this cyclization reaction, which was initially expected to follow the "rules" for electrocyclic ring closures, was probed in some detail. It is tentatively concluded that the stereochemistry in the products is not that expected from a conrotatory ring closure. Two diarylmethyl cations were also prepared. However, these did not cyclize.

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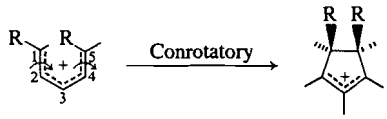
On a préparé une série d'alcools arylallyliques où le groupe aryl = diméthyl-2,6 phényle, mésityle, duryle ou pentaméthylphényle. Ces alcools en présence d'acides forts produisent des cations arylallyles. Dans certains cas on observe ces cations allyles et on les caractérise *in situ* en solution par la spectroscopie de rmn. Dans d'autres cas il se produit immédiatement une cyclisation, qui conduit de façon stéréospécifique à des séries de cations triényles bicycliques que l'on a entièrement caractérisés. On a établi de façon détaillée la stéréochimie de cette réaction de cyclisation, qui pensait-on devait suivre les règles de fermeture électrocyclique de cycles. On conclut que la stéréochimie des produits n'est pas celle attendue d'une fermeture conrotatoire de cycle. On a également préparé deux cations diarylméthyles. Toutefois ces cations ne se cyclisent pas.

[Traduit par le journal]

Introduction

The pentadienyl → cyclopentenyl (I → II) cation ring closure was first observed nearly 20 years ago (1), subsequently classified as an "electrocyclic" closure by Woodward and Hoffmann (2) and then, using methyl-substituted derivatives of I of fixed geometry, shown (3) to follow the predicted conrotatory mode.



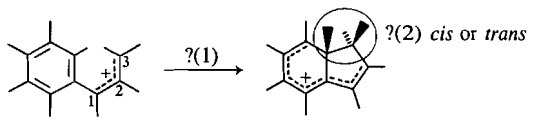
I II

This closure is irreversible, i.e. II is much more stable than I. The net bond energy changes involved in this can be very simply summarized:

[1] Pentadienyl resonance energy (R.E.) + π-bond → allyl R.E. + σ-bond

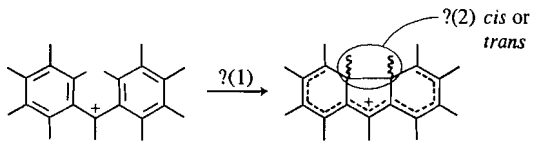
Thus, the main driving force is the favorable formation of a σ-bond from a π-bond (about 15–25 kcal/mol), the difference in the two R.E.'s expected to be small in comparison.

The present study involves extensions of the basic I framework, incorporating one and then two aromatic rings in place of the 1,2 and 4,5 "double bonds" of the pentadienyl unit. The possibility of a ring closure, analogous to I → II, can again be considered from two separate viewpoints, viz. is the open or closed cation the more stable and, secondly, in the event that ring closure does occur, what is the stereochemical outcome? The possible reactions are summarized below, the numbers in brackets referring to the above questions:



III IV

[2] Aryl R.E. + allyl R.E. + π-bond $\xrightarrow{?}$ trienyl R.E. + σ-bond



VI VII

[3] 2 × Aryl R.E. + π-bond $\xrightarrow{?}$ pentaenylic R.E. + σ-bond

Examples of diarylmethyl cations VI are numerous (4), but only a few arylallyl cations III have been studied (5–8). No previous stereochemical work on these cyclizations has been reported.

Results and discussion

The arylallyl cation III case

Our approach to studying a possible III → IV cyclization had to deal first with preventing the facile rearomatization of IV, a cation species previously unknown because of this. As it turned

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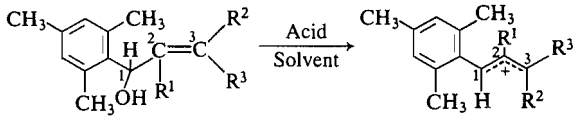
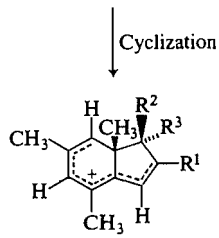
out, this was easily done by using aryl rings with both *ortho*-positions methyl-substituted. As implied, the cyclization of III to IV does occur in most of these cases, i.e. IV is thermodynamically more stable than III, in spite of the loss of aryl R.E. (see eq. [2]).

The first systems looked at were based on a mesitylene ring with the incipient allyl cation portion having either one or two methyl substituents, the one on C-3 being necessary to create the potential stereochemistry in IV. The starting alcohols **1–4** were prepared from mesitaldehyde and the corresponding vinyl lithium or from mesityl lithium and the α,β-unsaturated aldehyde.



1 $R^1 = R^2 = H$, $R^3 = CH_3$
2 $R^1 = R^3 = H$, $R^2 = CH_3$
3 $R^1 = R^2 = CH_3$, $R^3 = H$
4 $R^1 = R^3 = CH_3$, $R^2 = H$

III-1 $R^1 = R^2 = H$, $R^3 = CH_3$
III-2 $R^1 = R^3 = H$, $R^2 = CH_3$
Not directly observed
Not directly observed



IV-1 Not directly observed
IV-2 Not directly observed
IV-3 $R^1 = R^2 = CH_3$, $R^3 = H$
or
IV-4 $R^1 = R^3 = CH_3$, $R^2 = H$

Alcohols **1** and **2**, on addition to FSO_3H–SO_2ClF (1:4) at −120°C, yield the corresponding allylic cations III-1 and III-2, although III-2 was never obtained pure. At about −100°C, III-2 rearranges to the more stable III-1 geometry and this facile process no doubt occurs to some extent in the preparation of III-2. At much higher temperatures (35°C), cation III-1 cyclizes, but a rearranged indanyl cation V-1 was the first observed species (5) (destroying any stereochemistry inherent in IV).

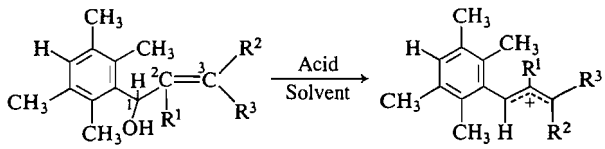
There are indications from previous literature examples (6) that substituting a methyl group at C-2 in III would increase the cyclization rate. This indeed was the case here and, on addition of alcohols **3** or **4** to the acid, only the cyclized ion (IV-3 or IV-4) was observed, even at temperatures as low as −120°C. The cyclized ion, by ^{13}C and ^1H nmr, appears to be a *single* stereoisomer and it is significant and disquieting that both alcohols should give the same cyclized ion.

Ideally, one would like to directly observe both cation structures III and IV *in the same system*. One possibility for the nonobservation of IV-1 might be that this ion is actually less stable than III-1. The corresponding durene-substituted alcohols **5** and **6** (analogous to **1** and **4**) were therefore prepared. Note that IV-5 and IV-6, compared to IV-4 (or a possible IV-1), have two extra methyl groups in stabilizing positions on the trienylic cation framework (denoted above in IV by ●). In any event, ionization of **5** leads cleanly to III-5 and this in turn cyclizes very cleanly to IV-5 at −70°C. Alcohol **6** (like **4**) yields only the cyclized ion IV-6, on ionization at −120°C. Both IV-5 and IV-6 appear to be *single* stereoisomers.

All of the observable III and IV ions were characterized as *in situ* solution species by ^1H and ^{13}C nmr spectroscopy and the data are given in Tables 1 and 2. Data for the further rearranged indanyl cations have been presented elsewhere (13).

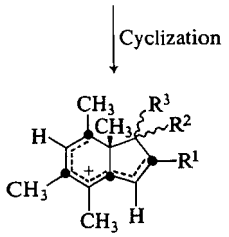
Thermodynamic aspects (question 1 in the Introduction)

Obviously IV-4, IV-5, IV-6 (and a pentamethyl species IV-8 to be discussed subsequently) are all more stable than the open arylallyl cations III. The situation with III-1 is less clear since the cyclization here proceeds directly to a rearomatized indanyl cation V-1. However, the observation that III-5 cyclizes to IV-5 at −70°C, whereas III-1 forms the indanyl cation V-1 only at +35°C, is a strong indication that III-1 is more stable than the unseen IV-1, since there is little kinetic reason why these very similar ions should not have cyclized (III →



5 $R^1 = R^2 = H$, $R^3 = CH_3$
6 $R^1 = R^3 = CH_3$, $R^2 = H$

III-5 $R^1 = R^2 = H$, $R^3 = CH_3$
Not directly observed



IV-5 $R^1 = R^2 = H$, $R^3 = CH_3$
IV-6 $R^1 = R^3 = CH_3$, $R^2 = H$

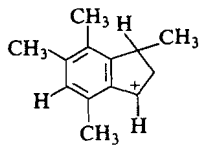
TABLE 1. ^{1}H nuclear magnetic resonance spectra of arylallyl cations III and trienylic cations IV

Cation	Solvent	Temperature °C	Position[a]					
			ortho	*meta*	*para*	1	2	3
III-1	FSO_3H–SO_2ClF	−60	2.60 2.68	7.16[b]	2.41	9.00[c]	7.73[d]	8.21[e] 2.49[f]
III-2	FSO_3H–SO_2ClF	−90	[g]	[g]	[g]	9.90[h]	[g]	[g]
III-5	FSO_3H–SO_2ClF	−100	2.51[i]	2.21	7.61	9.21[d]	7.84[c]	8.34[e] 2.51[i]
III-7	FSO_3H	−28	2.66	7.27[j]	7.75[k]	9.22[d]	7.78[c]	8.47[l] 2.55[f]

			Proton or methyl on carbon position							
			1	2	4	5	6	7	8	9
IV-3	FSO_3H–SO_2ClF	−80	2.40	7.12	2.06*	7.46*	2.19*	7.54*	1.25	1.35[m] 3.02[n]
IV-5	FSO_3H–SO_2ClF	−50	7.70[o]	7.20[p]	2.19*	2.40	6.95*	2.49*	1.24	1.40[q] 3.12[r]
IV-6	FSO_3H–SO_2ClF	−30	2.29*	7.00	2.12	2.29*	6.71	2.38	1.23	1.38[m] 2.98[n]
IV-8	96% H_2SO_4	0	2.19*	6.90	1.95*	2.19*	2.08*	2.32*	1.10	1.32[m] 2.94[n]

[a] Referenced indirectly to internal TMS in SO_2ClF = δ 0.00, except for IV-8, which is referenced to TMS/$CDCl_3$ = δ 0.00. Tentative assignments indicated by *.
[b] Broad, two peaks in some spectra.
[c] d, d, J = 13.6 and 13.6.
[d] d, J = 13.6.
[e] d, q, J = 13.6 and 6.5.
[f] d, J = 7.
[g] Peaks are overlapped with ion III-1 peaks.
[h] d, J = 14.
[i] Broad.
[j] d, J = 7.2.
[k] t, J = 7.2.
[l] d, q, J = 13.6 and 7.0.
[m] d, J = 7.0.
[n] q, J = 7.0.
[o] d, d, J = 5.50 and 1.80.
[p] d, d, J = 5.50 and 1.90.
[q] d, J = 7.3.
[r] q, J = 7.3, also coupled to H-1 and H-2.

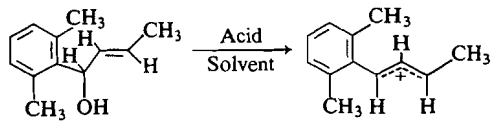
IV) at rather similar rates. This possible situation is presented diagrammatically in Fig. 1. Note that III-1 contains an extra *p*-Me stabilizing group, compared to III-5, while IV-5 has two extra stabilizing methyl substituents compared to the unseen IV-1.



V-1

In an attempt to find a possible case where III and IV might be in observable equilibrium (and thereby obtain proof for the Fig. 1 conjecture), the *m*-xylene system was prepared, starting with alcohol **7**. Cation III-7 should be similar in stability to III-5, but IV-7 should be less stable than IV-5 because the additional methyl groups in IV-5 are stabilizing (see IV-5 structure). However, addition of **7** to the acid solvent gave III-7, but this only yields an indanyl cation mixture on cyclization (+20°C). In spite of this negative result, we still believe that ions III and IV are similar in energy. This point is significant in our rationalization of the stereochemistry involved in the cyclization.

Cation IV is a benzenonium ion, normally considered a high energy intermediate in Friedel–Crafts alkylations. However, intermediates like IV always have a vanishly small concentration in normal alkylations *for kinetic reasons*, and one should not conclude anything about the actual thermodynamics of the benzenonium ion without some other kind of evidence.



7 III-7

Cyclization

Cation IV-7
not observed

TABLE 2. ^{13}C nuclear magnetic resonance spectra of arylallyl cations III and trienylic cations IV

Cation	Solvent	Temperature °C	Position[a]									
			ortho	*meta*	*para*	*ipso*	C-1	C-2	C-3	Methyls		
III-1[b]	FSO_3H–SO_2ClF	−50	156.2 161.0	133.5 135.2	168.3	133.5	193.2	137.1	184.8	21.1, 23.4, 24.6, 25.5		
III-5	FSO_3H–SO_2ClF	−110	153.1 158.5	140.2* 141.2*	155.1	138.1*	197.5	139.5	189.8	17.9, 20.7, 21.1 22.4, 26.6		
III-7	FSO_3H	−50	155.9 160.6	132.1 133.4	150.0	134.6	199.9	138.1	188.9	20.9, 25.3(×2)		
			C-1	2	3	4	5	6	7	8	9	Methyls
IV-3	FSO_3H–SO_2ClF	−80	210.3	133.6	214.0	136.2*	160.5*	135.7*	162.7*	71.3	58.0	10.5, 16.7, 20.1, 21.7, 36.3[c]
IV-5	FSO_3H–SO_2ClF	−50	190.3	132.5*	207.8	133.7	177.1*	131.2*	182.4*	69.0	52.0	12.5, 13.1, 22.8, 23.9, 37.8
IV-6	FSO_3H–SO_2ClF	−60	198.4	131.6*	209.0	132.3	178.7*	130.8*	184.8*	68.4	54.7	12.3, 13.8, 20.2, 23.0, 24.2, 38.1
IV-8	FSO_3H	−57	197.1	131.4*	207.7	132.4*	179.8*	135.4*	180.3*	68.7	55.1	12.7, 14.9(×2), 19.7, 19.9, 21.9, 38.3

[a] δ ppm, relative to internal $CFCl_3$ = δ 117.9. All multiplicities have been confirmed by off-resonance decoupling but a definitive assignment of closely spaced peaks of similar multiplicity is impossible. The tentative assignments are indicated by *.
[b] Line-broadening, described in the text, occurs at higher temperatures.
[c] A low field methyl carbon is present in all cases and is probably the methyl at C-8.

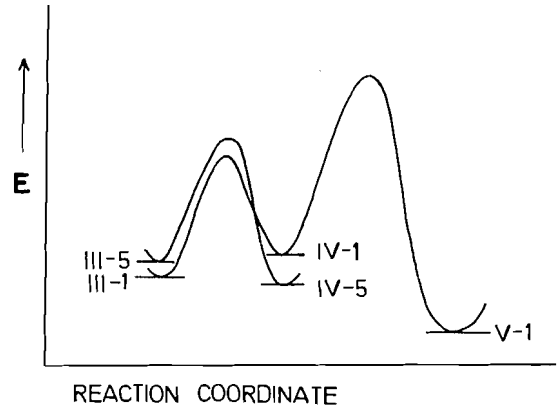
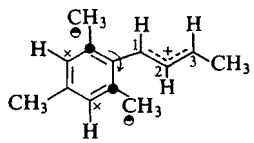


FIG. 1. This diagram is based on the assumption that the kinetics for III-1 → [IV-1] → V-1 would be similar to those observed for III-5 → IV-5 and that thermodynamic factors are responsible for the nonobservation of IV-1. III-1 is placed lower than III-5 because of the favorable *p*-Me group of the former. IV-5 is placed lower than IV-1 because of the two extra favorable methyl substituents.

Structure of the arylallyl cations

In cations III-1, III-5, and III-7, all three vicinal protons on the allyl unit have a 13.6 Hz coupling constant characteristic of a mutual *trans*-orientation. This leaves the aryl ring in the expected *anti*-orientation, as shown below:



⊖, ●, and × become equivalent by 180° rotation of the aryl ring

III-1

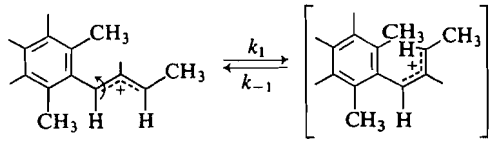
Cation III-2 likewise has a *trans*-orientation about C-1,C-2. The *cis*-orientation for H-2,H-3 in this ion follows because of the stereochemistry present in alcohol **2**, but the actual peaks for H-2 and H-3 are overlapped with others from ion III-1 and no $J_{2,3}$ constant could be obtained. The rearrangement of III-2 to III-1 is expected on stability grounds (9).

The bulky mesityl and duryl rings in III may not be entirely coplanar with the allyl part, but there is nevertheless a sizeable barrier for rotation about the C-1–aryl bond. This barrier can be determined for III-1, based on the line-broadening observed for the *ortho* and *meta* carbons (^{13}C nmr) or the *ortho*-methyl groups (^{13}C nmr). A barrier of 14 kcal/mol was estimated from the coalescence temperature of the aryl *meta* carbon peaks.

The cyclization of III to IV

Before discussing the cyclization of the arylallyl cations, one should comment briefly on the conformational requirements.

As in the pentadienyl cation case, the ring closure presumably proceeds via a geometric isomer of the arylallyl cation in which 180° rotation has occurred around the C-1,C-2 "bond" of the ground-state conformation (eq. [4]).

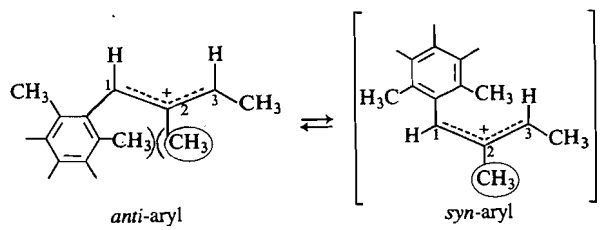
[4] 

anti-aryl *syn*-aryl

IV

This high energy *syn*-arylallyl cation cannot be planar, but this need not affect the chances for an electrocyclic ring closure, i.e. one governed by electronic rather than steric factors, since the previously-studied pentamethylpentadienyl cation cyclizations (which are nearly stereospecific) have very similar steric interactions in their "U" (reactive) conformations (3).

The arylallyl cations involving a 2-methyl substituent, e.g. from alcohols **3**, **4**, **6**, and **8**, could not be observed because of the enormous rapidity of the cyclization rate. For example, one can estimate that this substitution in the case of alcohols **5** and **6** is responsible for a minimum 10^3 increase in cyclization rate. The major source of this rate gain must involve a destabilization of the *anti*-arylallyl cation because it is now impossible to have a planar conjugated system, as illustrated below:



anti-aryl *syn*-aryl

The corresponding *syn*-arylallyl conformation is much less affected by this methyl group substitution and the overall effect is to reduce the energy difference between these ions. In this connection it should be noted that the present experiments do not tell one whether k_1 or k_2 in eq. [4] is rate-determining.

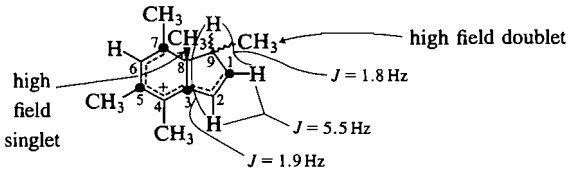
Alcohol **5**, where one can "see" both the arylallyl cation III-5 and the cyclized product IV-5, is the only case where the cyclization rate could be directly measured. The rate is first order and was experimentally measured by monitoring the loss of

^{1}H nmr peaks due to III-5 and the formation of IV-5 peaks, giving $k_{overall} = 5 \times 10^{-4}\,s^{-1}$ in FSO_3H at $-70°C$, $\Delta G^{\neq} = 15.6$ kcal/mol.

Although there is no direct evidence in these cyclizations that the *syn*-isomers exist as discrete species, we do have direct evidence for these from a *ring-opening* reaction to be discussed later in this paper.

Structural evidence for cations IV

In the ^{1}H nmr, the cyclized cations IV all show one high field (saturated) quaternary methyl and a high field methyl doublet. In IV-5, the two low field protons are coupled, $J = 5.5$ Hz, indicating a *cis*-orientation. The ^{13}C spectra are also very diagnostic, showing seven low field carbons. The four carbons formally sharing the positive charge



IV-5

(● in the structure above) form one group and the other three a higher field group. In the specific case of IV-5, three of the lower field group are quaternary and one is CH, while the upper field group has one quaternary and two CH carbons (see Tables 1 and 2).

The visible spectrum of IV-8 has $\lambda_{max} = 483$ nm, $\varepsilon_{max} = 9400$, as the longest wavelength absorption, in good agreement with 473 nm for an acyclic trienylic cation (10).

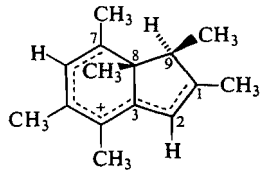
Stereochemistry of cyclized ions IV (question 2 – Introduction)

As previously noted, the ^{13}C nmr spectra of IV-4, IV-5, IV-6, and IV-8 are consistent with the initial formation of a *single* stereoisomer. To try to determine this stereochemistry, the following methods were tried.

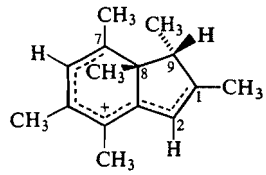
1. Assuming the product was one of kinetic control, we tried to equilibrate the ion at C-9 to at least produce *both* stereoisomers. This kind of equilibration works for the simple cyclopentenyl cations (11), e.g. 1,2,3,4,5-pentamethylcyclopentenyl cation eventually forms a *trans*/*cis* ratio of 3.9, starting from either relatively pure isomer. The usual equilibration mechanism would involve deprotonation–reprotonation at C-9 and the rate for such reactions becomes faster the weaker the acid solvent (stronger bases present) (12).

However, cation IV-6 resolutely refused to do anything, even when acids as weak as aqueous trifluoroacetic acid were used. That an acid–base equilibration reaction *was not* occurring was clear, because when CF_3COOD–D_2O mixtures were used, no D appeared at C-9 in the ion. Eventually, if one weakens the acid solvent too much, degradation occurs but with no sign of any second equilibration partner.

2. Nuclear Overhauser enhancement nmr experiments were attempted on ion IV-6; the two possible geometries are shown below:

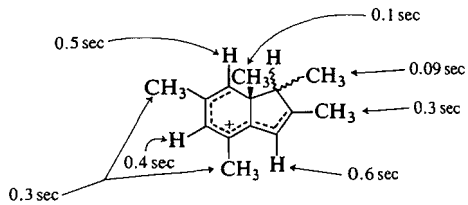


IV-6A



IV-6B

In IV-6B, the C-7 and C-9 methyl groups are quite close in space. However, using degassed samples of IV-6 in D_2SO_4 solvent (or IV-4 in DSO_3F solvent), no measurable nOe effects were found for these methyls. A subsequent T_1 measurement on several of the ions revealed that the methyl groups in question have very short relaxation times (shown below for IV-4).



IV-4 T_1 relaxation times (−55°C, $DFSO_3$)

The usual nOe effects could be obtained on protonated DMF in D_2SO_4 or DSO_3F and these protons also have much longer T_1's, for example 1.3, 1.2 s for the high and low field methyls and 0.8 s for the methine proton in D_2SO_4 at 22°C. At the same temperature in DSO_3F, T_1 values are 3.1, 2.8, and 5.0 s. The short T_1 problem in IV-4 likely stems from the large size of the ion, resulting in correlation times very suitable for T_1 relaxation. It is significant in this regard that the quaternary methyl has a very short relaxation time and this protrudes from the top of the nearly planar surface formed by the remaining atoms.

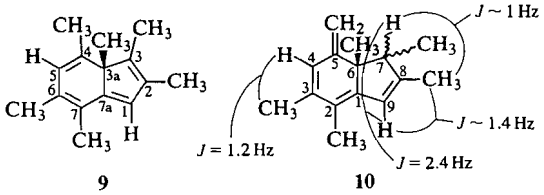
3. Attempts to obtain crystalline salts of IV-8, suitable for X-ray work, were unsuccessful. The ion solutions are highly colored, making visual observation of crystal formation difficult. The usual material obtained was amorphous.

Cation IV quenching studies

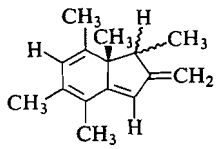
Quenching sulfuric acid solutions of IV-6 in

H_2O–$(CH_2OH)_2$–NaOH at ca. −20°C results in a near quantitative yield of proton-elimination products, obtained as an oil. This material (from ^1H and ^{13}C nmr) is mainly a mixture of two compounds. The major isomer is a 3aH-indene **9**, involving proton loss at C-9 in the ion. This unfortunately destroys the stereochemistry inherent in the system and is thus of no use to us. The spectral and chemical properties of **9**, as well as synthetic possibilities, are discussed elsewhere (13).

The minor component is the more interesting since it shows both the high field quaternary methyl *and* the high field doublet methyl which were present in the ion. In principle, one can eliminate a proton from the termini of IV-6 in two ways, viz. conjugated tetraenes **10** or **11**, respectively. However, a detailed analysis of the ^1H spectrum, particularly the coupling constants, favours **10**. This is discussed more fully in the "pentamethylbenzene" analog (ion IV-8).

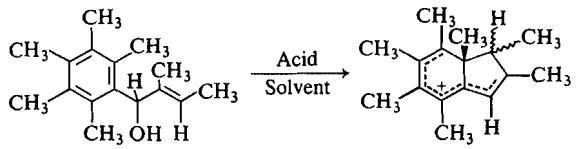


9 **10**



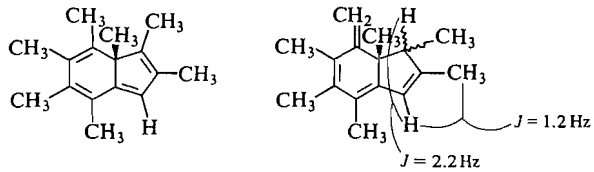
11

Attempts to separate **9** and **10** were unsuccessful because both compounds are very sensitive. Some chemical degradation studies were attempted on the mixture but no useful results were obtained. One can convert **9** into a ring-opened ketone (13), while leaving **10** at least partly untouched. This helps in assigning the nmr spectrum of **10**, but the isolation of pure **10** still proved impossible in our hands. We also sought quenching procedures designed to get better yields of **10**, but to no avail. However, it was discovered that the pentamethylbenzene analog, cation IV-8, could be quenched to give mainly the exocyclic tetraene component. Cation IV-8 is produced very cleanly from alcohol **8**.

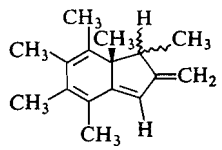


8 IV-8

Quenching IV-8 leads to a mixture which is mainly an exocyclic tetraene, together with a smaller amount of the 3aH-indene **12** (13). The exocyclic tetraene was assigned the structure **13** rather than **14** on the basis of the ^1H nmr coupling constants observed (also applied to the assignment of **10** vs. **11**).

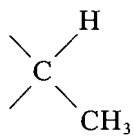


12 **13**



14

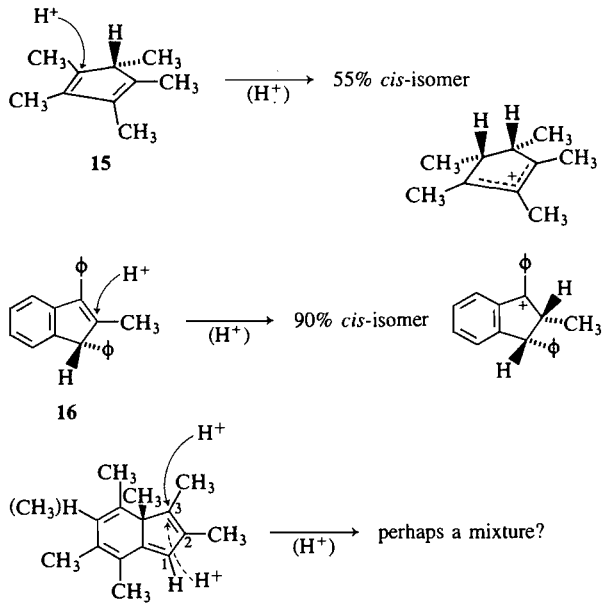
Compounds **12** and **13** were obtained as an oil and attempts to separate these sensitive substances by chromatography or low temperature crystallization were unsuccessful. The apparently ready conversion of **13** to **12** makes chemical degradation studies difficult. The primary attempt in these degradation studies was to first convert the $=CH_2$ in **13** to $=O$, which could perhaps be obtained crystalline itself or as an adduct (then X-ray analysis). Numerous ozonolysis and periodic acid – OsO_4 reactions always led to crude mixtures in which the saturated



functionality was very weak or missing in the ^1H nmr spectra of the crude products. In attempts to convert $=CH_2$ to $-CH_2OH$, 9-BBN proved unreactive. The major problem is probably that the $=CH_2$ group is well-shielded by the other methyl substituents and reactions at other sites or **13** → **12** rearrangements intervene.

Attempts to determine the stereochemistry in IV by kinetically-controlled protonation of 3aH-indenes 9 or 12

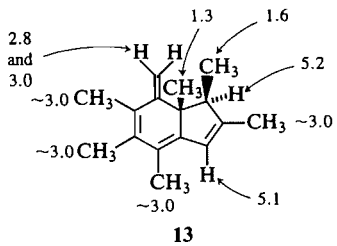
With pentamethylcyclopentadiene **15** (11) or 1,3-diphenyl-2-methylindene **16** (6), protonation occurs under kinetic control and results predominantly in that cation isomer in which the proton approaches from the least hindered side, giving in these cases the less-stable *cis*-isomer. In the case of **9**, it is not immediately obvious which side is the more hindered, but the protonation in H_2SO_4 should defi-



nitely be kinetically controlled (earlier in this paper it was remarked that no H–D exchange occurs in any of the acid solvents). However, protonation in H_2SO_4 results in only one cation being formed, the *same* one as produced in the original cyclization reaction. Protonation does occur at C-3 because, in CF_3COOD, the high field methyl doublet of IV-6 is at least partially collapsed.

Possible stereochemical differentiation by nOe and T_1 studies on the tetraene ***13***

T_1 values (in seconds) for degassed samples of **13**

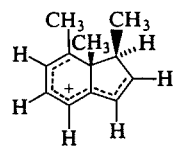


13

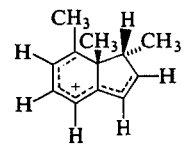
in $CDCl_3$ are given below. Both aliphatic methyl groups are seen to have rather short T_1's. The nOe experiments were tried at both 200 and 400 MHz ^1H fields. At 400 MHz, there is virtually no enhancement of the quaternary methyl on irradiation of the methyl doublet and vice versa. Conversely, there is no nOe effect (200 MHz) between the methyl doublet and either of the $=CH_2$ protons.

Molecular orbital calculations

Further to our attempts to assign the stereochemistry to these ions, semiempirical MINDO/3 calculations were performed on the model cations IV-9A and IV-9B (corresponding to IV-5 with removal of C-4 and C-5 methyl groups). The geometries were fully optimized except for hydrogen dihedral angles in methyl groups. In addition, all methyl C—H bonds were made equal and, separately, all C_{sp^2}—H bonds were kept equal. These calculations are relevant if one assumes that the observed IV-cations might be products of thermodynamic rather than kinetic control (see Discussion). The total energies (in kcal/mol) for IV-9A and IV-9B are given next to the structure.



IV-9A 217.87 kcal/mol



IV-9B 217.91 kcal/mol

Structure IV-9A is shown in Fig. 2. These calculations suggest the two ions to be essentially of equal energy and are of no use, in a total energy sense, in helping one assign the unknown stereochemistry. However, the optimized geometries do offer some help in interpreting the H-9,H-1 coupling constant in ion IV-5.

The H-9,H-1 vicinal coupling constant in ion IV-5

The H-1,H-2 coupling in ion IV-5 is 5.5 Hz, typical of *cis* double bond coupling in five-membered rings, and this value can be used to calibrate the Karplus curve. The observed H-9,H-1 coupling of 1.8 Hz corresponds to a dihedral angle of about 52°. The calculated dihedral angles in IV-9A and IV-9B are 79 and 47°, respectively. Clearly, ion IV-9B is favored on this basis.

The Karplus relationship generally cannot be used to any degree of "exactness" but the two dihedral angles calculated in this case are sufficiently

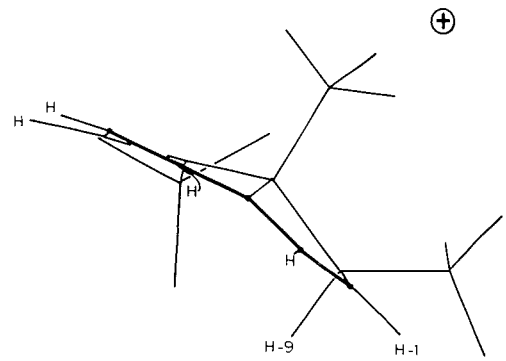


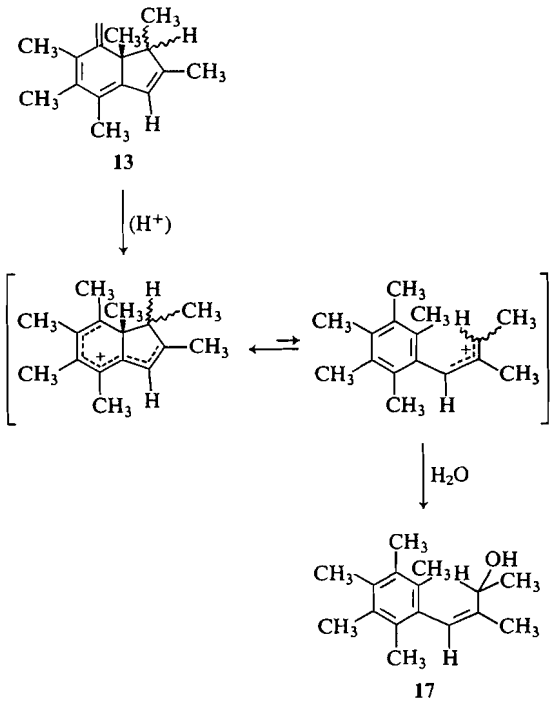
FIG. 2. Computed structure (MINDO/3) for the model cation IV-9A. Note that the H-9,H-1 dihedral angle of 79° is not consistent with the experimental nmr data, and thus the IV-9B structure is favored.

different that one has some confidence in the assignment.

Ring-opening reaction of tetraene 13

This reaction is not relevant to the stereochemistry problem, but is very relevant to the cyclization mechanism shown in eq. [4]. The tetraene mixture from the quench of ion IV-8 (mainly **12** and **13**), on standing in dilute aqueous acid (ca. pH = 1), is fairly rapidly converted to the alcohol **17**, whose structure has been proven (13).

[5]



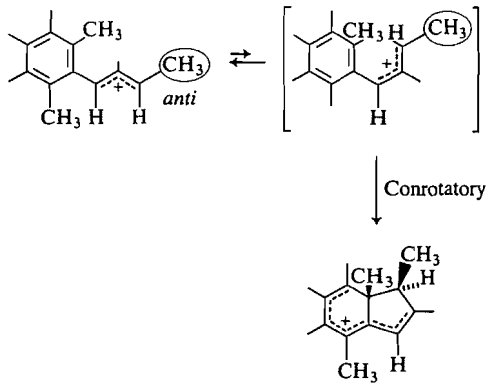
Two points are significant here: (1) the *syn*-arylallyl cation is the obvious precursor of **17**, and thus the existence of this intermediate is confirmed, and (2) the energy separation between the closed and open ions is likely small, a conclusion also reached on other grounds.

Discussion of the arylallyl cation results

Simple HMO theory predicts a conrotatory closure for the aryallyl cations. With a ground-state *anti*-methyl substituent as a marker, this leads to a predicted *cis*-dimethyl geometry (eq. [6]) in the cyclized ions.

Experimentally, one finds only one isomer being produced. We assume that this single isomer probably has the same stereochemistry in all of the IV-ions, although there is no complete proof that this is so. In addition, the evidence for a single ion is based on the premise that the ^{13}C and ^{1}H nmr

[6]



spectra would not be absolutely identical for the two stereoisomers.

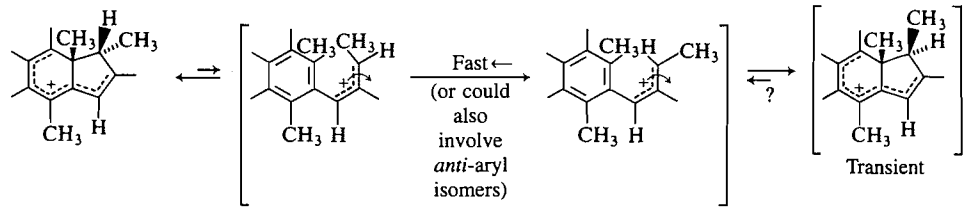
The argument against a conrotatory ring closure in our examples is that both alcohols **3** and **4**, which have *syn*- and *anti*-methyl substituents, respectively, give the same single cyclic ion IV product. It is possible of course that III-3 and III-4 are rapidly interconverted before cyclization, since neither ion is directly observed. However, the stable isomer of the two is III-4 and this should produce the *cis*-dimethyl geometry. In the case of ions III-1 and III-2, the corresponding *syn* → *anti* rate is measurable and is indeed relatively fast.

All in all, it seems most probable that, in spite of the MO calculations, one stereoisomer, probably the *trans*-dimethyl isomer, is significantly more stable than the other and that the stereochemistry of our cyclization reaction is governed by this thermodynamic factor.

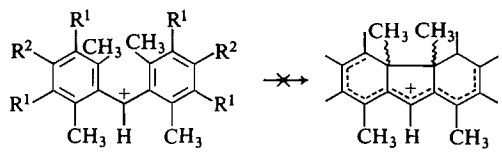
Even allowing for the above, there are excellent precedents for expecting a kinetically controlled protonation of the isoindenes **9** and **12**, which should have given a IV mixture containing both stereoisomers. Any possible isomerization of one stereoisomer to the other has already been shown not to involve a deprotonation–reprotonation mechanism, but the mechanism shown in eq. [7] could conceivably allow a rapid equilibration to the more stable IV-isomer and is illustrated for the case where the *trans*-dimethyl isomer is assumed to be the more stable. The key feature is that the "open" and "closed" ions be similar in energy, a conclusion already reached from several pieces of evidence.

The diarylmethyl cations

The diduryl- and dimesitylmethyl cations VI-1 and VI-2 were produced from the known alcohols (14, 15) and chemical shift data (^{1}H and ^{13}C) are given in Tables 3 and 4. In CF_3COOH, the cations have λ_{max} = 510 and 526 nm, ε_{max} = 23 300 and 35 700, respectively. These ions show no indication

[7] 

of cyclizing, even after prolonged storage at 20°C. In view of the previous conclusions regarding arylallyl cations, one would confidently predict that the cyclized ions VII would be of high energy relative to VI.



VI-1 $R^1 = CH_3$, $R^2 = H$
VI-2 $R^1 = H$, $R^2 = CH_3$

VII

Discussion of the diarylmethyl cation results

Only when rearomatization of VII can readily occur would it be possible to carry out a cyclization of VI (via VII as a high-energy intermediate). An example of this is the well-known conversion of triphenylmethanol into 9-phenylfluorene (16), carried out in strong acid. Photochemical cyclizations of triarylmethyl cations are also known (17). A mass-spectral study (18) of diphenylmethyl bromide has been interpreted in terms of a diphenylmethyl cation cyclization, to give an analog of VII, which subsequently loses H_2. On this basis, the cyclization stereochemistry was postulated to be the *cis* di-H analog of VII (a disrotatory cyclization), since the concerted loss of H_2 from the *trans* isomer was considered unlikely. However, these results are very indirect and interpretation in terms of specific structures is conjectural.

Conclusions

With respect to the questions asked in the Introduction: (1) the cyclization of arylallyl cations is generally favorable, but there is evidence that the *energy differences are small*; (2) the cyclization product consists of only *one stereoisomer*, most probably the *trans*-dimethyl structure IV-B. However, there are still a number of unanswered mechanistic questions in this connection and (3) diarylmethyl cations VI do not cyclize to cation VII and are undoubtedly thermodynamically more stable than VII.

TABLE 3. ^1H nuclear magnetic resonance spectra of diarylmethyl cations

Cation	Solvent	Temperature °C	Position[a] *ortho*	*meta*	*para*	$\overset{+}{C}H$
VI-1	FSO_3H	25	2.65	2.65	8.00	10.66
VI-2	FSO_3H	25	2.73	7.53	2.83	10.20

[a]Chemical shifts in δ ppm relative to external TMS in TMS-d_{12}.

Experimental

The nmr spectra were obtained on Varian models HA-100 and XL-200 and Bruker model WH-90 spectrometers. Electronic spectra were obtained in 96% H_2SO_4 solution on a Cary 219 spectrophotometer. Constant temperature runs (and kinetic measurements) were obtained on the Bruker instrument using a previously described calibration procedure (19). The nmr spectra of all neutral compounds were measured in $CDCl_3$ or $CFCl_3$ solutions and are quoted relative to internal TMS (δ = 0.00).

All lithium reactions were carried out under a nitrogen or argon atmosphere. Boiling points and melting points are uncorrected.

Ion preparations (FSO_3H–SO_2ClF, FSO_3H, 96% H_2SO_4, CF_3COOH)

For ^1H nmr work, the alcohol (50 mg) in a small amount of $CFCl_3$ was added by pipette to 0.5 mL of 1:4 v/v FSO_3H–SO_2ClF solutions contained in a 5 mm nmr tube and cooled to ca. −125°C using a pentane–N_2 slush bath. The solution was stirred with a Pt wire during the alcohol addition. All of the ions in this work are very highly colored. For ^{13}C nmr spectra, about 200 mg of alcohol was used (10 mm tubes) in ca. 2 mL of the acid solution. About 6000 accumulations were needed for good signal-to-noise spectra, usually employing a sweep width of 9000 Hz on the Bruker WH-90. Off-resonance spectra were also obtained to aid in the assignments. For pure FSO_3H solvent, the alcohol, in a very small amount of $CDCl_3$, was added with stirring to the FSO_3H, the latter in an nmr tube and cooled at ca. −80°C in a Dry Ice bath. Sulfuric acid solutions were prepared by adding the acid and an equal volume upper pentane layer to a 5 mL flask. To the stirred mixture at −10 to 0°C was added dropwise the alcohol dissolved in a small amount of pentane. After a few minutes, the lower layer ion solution was removed by pipette and transferred to nmr tubes. For CF_3COOH solutions, the solid alcohol was added directly in small portions to the stirred acid at 0°C.

For FSO_3H–SO_2ClF solutions, the ^{19}F signal of SO_2ClF was used as a lock. For FSO_3H solutions, a 2 mm (^1H) or 5 mm (^{13}C) insert of TMS-d_{12} was used as lock. For sulfuric acid solutions, either the TMS-d_{12} or a dimethylether-d_6 insert was used for locking, while CF_3COOH solutions were locked to the ^{19}F of the acid. In FSO_3H–SO_2ClF solutions, $CFCl_3$ serves as an internal ^{13}C reference (δ 117.9), while in the ^1H spectra, a small amount of TMS in the TMS-d_{12} served as a reference. The dimethyl ether-d_6 insert also contained a small amount of TMS. The δ positions of the various references, relative to TMS in $CDCl_3$ or SO_2ClF, have been determined for both iron magnet and supercon field configurations.

TABLE 4. ^{13}C nuclear magnetic resonance spectra of diarylmethyl cations

Cation	Solvent	Temperature °C	Position[a]							
			ortho	*meta*	*para*	*ipso*	*o*-CH_3	*m*-CH_3	*p*-CH_3	$\overset{+}{C}H$
VI-1	CF_3COOH	25	148.5	140.5	142.6	142.6	18.9*	17.5*	—	193.0
VI-2	CF_3COOH	25	151.9	133.7	163.6	139.3	20.7	—	22.7	187.6

[a] In ppm relative to external TMS = δ 0.0, * indicates tentative assignments.

For the acid–base exchange attempts, deuterated acids CF_3COOD and CF_3COOD–D_2O solvents were used (^1H nmr spectra), employing the same experimental techniques.

For the reprotonation studies on the **9**, **10** or **12**, **13** mixtures (attempted kinetic protonation), FSO_3H or H_2SO_4 solvents were used, the former using a $CDCl_3$ solution, the latter using the pentane extraction method. The deuterated acid used in these studies was CF_3COOD.

The arylallyl alcohols were prepared by adding known aldehydes to known aryl or vinyl lithium compounds (prepared *in situ*). The crude alcohols were purified by vacuum distillation or recrystallization, or both. The ^1H nmr characterization does not include the OH proton.

E-*1-Mesityl-2-buten-1-ol* ***1***

From mesityl lithium and crotonaldehyde, the crude product directly recrystallized from pentane, 96% yield, mp 57–58°C; ^1H nmr: 1.66 (d, J = 7, C-3 methyl), 2.19 (*p*-CH_3), 2.32 (*o*-CH_3), 5.3–5.9 (complex, protons on C-1, 2, and 3), 6.76 (*m*-H); ^{13}C nmr: 17.7 (C-3 methyl), 20.6 (*o*-CH_3), 20.7 (*p*-CH_3), 71.6 (C-1), 126.5 (C-3), 130.0 (*meta*), 131.7 (C-2), 135.7 (*ipso*), 136.3 (*ortho*), 136.7 (*para*). *Anal.* calcd. for $C_{13}H_{18}O$: C 82.1, H 9.5; found: C 81.9, H 9.3.

Z-*1-Mesityl-2-buten-1-ol* ***2***

Mesitaldehyde was added to the lithium reagent from *Z*-1-bromo-1-propene. The crude solid product could not be further purified since all attempts to recrystallize the alcohol from pentane resulted in an allylic rearrangement. However, the ^1H and ^{13}C nmr spectra of the crude alcohol indicated that it was nearly pure. Yield 88%, mp 45–46°C; ^1H nmr: 1.62 (d, J = 7, C-3 methyl), 2.18 (*p*-CH_3), 2.35 (*o*-CH_3), 5.51 (complex, H-3), 5.82 (complex H-1 and H-2), 6.74 (*m*-H); ^{13}C nmr: 13.2 (C-3 methyl), 20.7 (*o*- and *p*-CH_3's), 67.1 (C-1), 126.1 (C-3), 130.1 (*meta*), 132.1 (C-2), 136.1 (*ipso*), 136.2 (*ortho*), 136.7 (*para*). *Anal.* calcd. for $C_{13}H_{18}O$: C 82.1, H 9.5; found: C 82.2, H 9.5.

Z-*1-Mesityl-2-methyl-2-buten-1-ol* ***3***

Mesitaldehyde was added to the lithium reagent from *Z*-2-bromo-2-butene, 75% yield, bp 95–98°C/0.05 Torr. The nmr spectrum (see below) indicates that ca. 10% of the *E*-isomer is present, ^1H nmr: 1.54 (d, J is hidden, C-3 methyl), 1.56 (C-2 methyl), 2.18 (*p*-CH_3), 2.28 (*o*-CH_3), 5.33 (quart., J = 7, H-3), 5.70 (H-1), 6.71 (*m*-H); ^{13}C nmr: 14.2 (C-3 methyl), 21.5 (*o*-, *p*-, and C-2 methyls), 71.9 (C-1), 123.1 (C-3), 130.7 (*meta*), 136.6, 137.1, 137.3 (*ortho*, *para*, *ipso*, C-2). *Anal.* calcd. for $C_{14}H_{20}O$: C 82.3, H 9.9; found: C 82.0, H 9.8.

E-*1-Mesityl-2-methyl-2-buten-1-ol* ***4***

Tiglaldehyde was added to mesityl lithium, the crude product directly recrystallized, from pentane, 94% yield, mp 63–64°C; ^1H nmr: 1.56 (d, J = 7, C-3 methyl), 1.48 (C-2 methyl), 2.16 (*p*-CH_3), 2.22 (*o*-CH_3), 5.32 (H-1), 5.37 (quart., J = 7, H-3), 6.68 (*m*-H). Considerable long range coupling is present in the C-1, 2, and 3 methyls and protons; ^{13}C nmr: 13.0 and 13.6 (C-2 and C-3 methyls), 20.5 (*o*-CH_3), 20.7 (*p*-CH_3), 74.0 (C-1), 118.4 (C-3), 129.9 (*meta*), 135.3 (C-2), 135.4 (*para*), 136.7 (*ipso*), 137.1 (*ortho*). *Anal.* calcd. for $C_{14}H_{20}O$: C 82.3, H 9.9; found: C 82.3, H 9.9.

E-*1-Duryl-2-buten-1-ol* ***5***

Crotonaldehyde was added to duryl lithium and the residue purified by vacuum distillation, bp 120–122°C/0.05 Torr, mp 79–80°C, yield 83%; ^1H nmr: 1.60 (d, J = 7, methyl on C-3), 2.15 (*m*-CH_3), 2.20 (*o*-CH_3), 5.26–5.94 (multiplet, H-1, 2, 3), 6.80 (*p*-H); ^{13}C nmr: 16.2 (*m*-CH_3), 17.7 (C-3 methyl), 20.5 (*o*-CH_3), 71.8 (C-1), 126.6 (C-3), 131.2 (*para*-H), 132.2 (C-2), 132.4 (*ortho*), 134.5 (*meta*), 138.8 (*ipso*). *Anal.* calcd. for $C_{14}H_{20}O$: C 82.3, H 9.9; found: C 81.9, H 9.8.

E-*1-Duryl-2-methyl-2-buten-1-ol* ***6***

Tigaldehyde was added to duryl lithium and the residue purified by vacuum distillation, bp 128–131°C/0.15 Torr, mp 45–46°C, yield 85%; ^1H nmr: 1.54 (d, J = 7, C-3 methyl), 1.55 (C-2 methyl), 2.13 (*o*- and *m*-CH_3's), 5.32 (quart., J = 7, H-3), 5.52 (H-1), 6.83 (*p*-H). Considerable long range coupling is present in the C-1, 2, and 3 methyls and protons; ^{13}C nmr: 13.1 and 13.7 (C-2 and C-3 methyls), 16.1 (*m*-CH_3), 20.5 (*o*-CH_3), 74.5 (C-1), 118.6 (C-3), 131.0 (*p*-H), 133.1 (C-2), 134.3 (*meta*), 136.0 (*ortho*), 138.6 (*ipso*). *Anal.* calcd. for $C_{15}H_{22}O$: C 82.5, H 10.2; found: C 82.0, H 10.0.

E-*1-[1-(2,6-Dimethylphenyl)]-2-buten-1-ol* ***7***

Crotonaldehyde was added to the lithium reagent from 2-bromo-*m*-xylene. The crude solid was recrystallized from pentane, mp 49–50°C, yield 88%; ^1H nmr: 1.65 (d, J = 7, C-3 methyl), 2.35 (*o*-CH_3), 5.30–5.90 (mult., H-1, 2, 3), 6.82–7.00 (mult., *m*-H, and *p*-H); ^{13}C nmr: 17.7 (C-3 methyl), 20.8 (*o*-CH_3), 71.6 (C-1), 125.9 and 127.4 (C-3 and *para* C), 129.5 (*meta*), 132.4 (C-2), 136.6 (*ortho*), 139.1 (*ipso*). *Anal.* calcd. for $C_{12}H_{16}O$: C 81.8, H 9.2; found: C 81.9, H 9.3.

E-*1(1-Pentamethylphenyl)-2-buten-1-ol* ***8***

Tiglaldehyde was added to the lithium reagent from pentamethylbromobenzene. The latter required 24 h reflux (diethyl ether solvent) to form. Distillation of the crude residue, bp 148–149°C/0.05 Torr and recrystallization from pentane gave 52% yield of the pure alcohol, mp 82–83°C; ^1H nmr: 1.55 (d, J = 7, C-3 methyl), 1.61 (C-2 methyl), 2.20 (*o*-, *m*-, and *p*-methyl), 5.1–5.75 (H-1 and H-3); ^{13}C nmr: 13.1, 13.6 (C-2 and C-3 methyls), 16.6 and 17.1 (*o*- and *m*-CH_3), 16.9 (*p*-CH_3), 74.7 (C-1), 118.3 (C-3), 132.8, 133.0 (*meta* and C-2), 133.7 (*para*), 136.9, 137.0 (*ortho* and *ipso*). *Anal.* calcd. for $C_{16}H_{24}O$: C 82.75, H 10.3; found: C 82.7, H 10.6.

2,3,6,7,8-Pentamethyl-5-methylenebicyclo[4.3.0]nona-1,3,8-triene ***10***

This compound, in a mixture together with isoindene **9** (ca. 1:2–3 of **10**/**9**), was obtained as an oil. It was characterized by ^1H nmr spectroscopy: 6.09 (1H, mult., H-9), 5.82 (1H, mult., H-4), 4.69 and 4.80 (each 1H), singlets, $=CH_2$), 2.56 (1H, broad quart., J = 7, H-7), 1.74 (3H) and 1.80 (6H), (CH_3's at C-2, 3, and 8), 1.05 (3H, doublet, J = 7, CH_3 at C-7), 0.89 (3H, singlet, CH_3 at C-6). The nmr assignments are aided by being able to convert **9** into a ketone while leaving **10** intact (13). Long range coupling

constants were obtained by decoupling studies and are shown on structure **10**.

2,3,4,6,7,8-Hexamethyl-5-methylenebicyclo[4.3.0]nona-1,3,9-triene ***13***

This compound, in a mixture with isoindene **12** (ca. 2–3:1 of **13**/**12**), was obtained as an oil and characterized by ^{1}H nmr spectroscopy: 6.07 (1H, mult., H-9), 4.94 and 4.89 (each 1H, singlets, $=CH_2$), 2.6 (1H, broad quart., J = 7, H-7), 1.82 and 1.81 (9H, CH_3's at C-2, 3, 4), 1.74 (3H, CH_3 at C-8), 1.09 (3H, doublet, J = 7.2, CH_3 at C-7), 0.85 (3H, singlet, CH_3 at C-6). Long range coupling constants were obtained by decoupling studies and are shown on structure **13**.

Quenching experiments

Several experiments in which CF_3COOH, 96% H_2SO_4, and FSO_3H were employed as acid solvents for preparing the ions showed that 96% H_2SO_4 is the most convenient of these for quenching in base to give neutral products. Cations IV-6 and IV-8 were employed in these quenching studies. The only drawback to using 96% H_2SO_4 is the relatively high melting point. Cation IV-4, for example, is stable only up to about −30°C and therefore cannot be prepared in 96% H_2SO_4. The best quenching procedure was to add the sulfuric acid solution (typically 1 g of ion/10 mL of acid solvent) dropwise at 0°C to a vigorously stirred mixture of 60 g of sodium carbonate in 200 mL of water, 200 mL of ethylene glycol, and 200 mL pentane, cooled to −20°C. After warming to 20°C, the pentane layer was separated, a further pentane extraction made, and the combined layers washed with sodium carbonate solution and then water, and dried over anhydrous K_2CO_3. Removal of the solvent gave >90% recovery of organic material. In some cases, the main product is an alcohol (by nmr) but this alcohol is very unstable and readily dehydrates to the alkene material which is more often the direct first observed product. Other quenching procedures using NH_2^-/NH_3, a CH_2Cl_2/Na_2CO_3 suspension, or aqueous pyridine as bases were unsatisfactory.

Molecular orbital calculations

The standard MINDO/3 procedure of Dewar and co-workers was used (20). A PLUTO plotting routine (21) was used to construct the diagram in Fig. 2.

Nuclear Overhauser effect experiments

The 400 MHz measurements were performed at the University of Alberta on a Bruker WH-400 spectrometer using a subtraction routine to plot only difference spectra. The 200 MHz experiments were carried out on a Varian XL-200 using the subtraction routine No. 28 from the Varian library of pulse sequences for this instrument.

T_1 *experiments*

The inversion–recovery method was used, with automatic data processing by the XL-200 nmr spectrometer. Standard deviations were usually less than ±10%. Samples were deoxygenated by nitrogen purging for several hours.

Crystalline salt attempts

The alcohol **8** was treated for several hours at 0°C with an excess of PCl_5. The solid was filtered off and to the resulting solution was added a suspension of $AlCl_3$ in CH_2Cl_2 (1:1 molar ratio of presumed organic chloride/$AlCl_3$). An immediate reddish-black color developed and the solution was filtered under nitrogen. Partial evaporation of the CH_2Cl_2 usually gave a dark amorphous solid.

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