Indanyl Cations. Their Stereoselective Formation from Acyclic Phenyl-Substituted Allylic Cations and Temperature-Dependent Rearrangements

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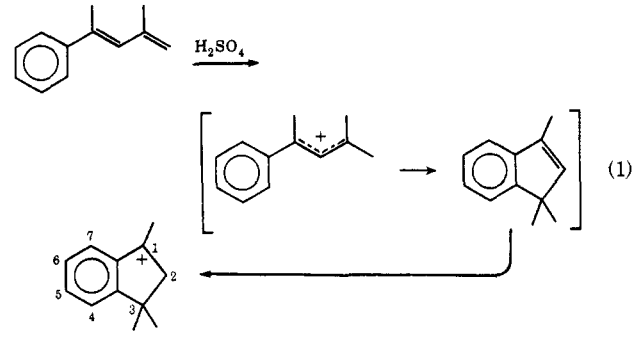
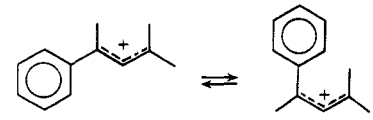
Abstract: The 1,3-diphenylbutenyl cation (**2a**) and the 1,1,3-triphenyl-2-propenyl cation (**2b**) have been directly observed by nmr spectroscopy after their generation from their respective allylic alcohols (**1a** and **1b**) in FSO_3H at $-70°$. These are the first acyclic, phenyl-substituted, allylic cations to be reported. On warming the acid solutions, cyclization to indanyl cations was observed. A series of 12 phenyl-substituted allylic alcohols was prepared and studied in both FSO_3H at low temperatures and H_2SO_4 at room temperature. In all cases the acyclic allylic cations cyclized to transient indenes which protonated to give indanyl cations. Cyclization always proceeded from the least substituted end of the allylic system. Several indanyl cations underwent further temperature-dependent rearrangements to new indanyl cations. The rearrangements were followed by nmr, deuterium labeling, deuterium exchange, and temperature-dependent quenching studies. The stereoselective protonation of three transient indenes was observed. For example, the 1,2,3-triphenyl-2-butenyl cation cyclizes in FSO_3H at $-70°$, to 1-methyl-2,3-diphenylindene (**3d**), which undergoes initial kinetic protonation to give the *cis*-1-methyl-2,3-diphenylindanyl cation (**4d**). Eventually *trans*-**4d**, the thermodynamic product, is formed. On continued warming, further rearrangement to the *trans*-1,2-diphenyl-3-methylindanyl cation (**5d**) occurs *via* a 1,3-hydride shift. Interestingly, the *trans*-1,2-dimethyl-3-phenylindanyl cation (**4c**) rearranges to the *trans*-1-phenyl-2,3-dimethylindanyl cation (**5c**) *via* two successive 1,2-hydride shifts.

Both cyclic and acyclic alkyl-substituted allylic cations are stable in strong mineral acids (*i.e.*, concentrated H_2SO_4, FSO_3H, SbF_5–FSO_3H, etc.) and have been directly observed and studied by spectroscopic methods, especially pmr.[2-6] However, no successful observations of acyclic phenyl-substituted allylic cations have yet appeared in the literature.[7] In an attempt to generate the 2-phenyl-4-methylpentenyl cation in H_2SO_4, Deno, Pittman, and Turner[8] observed only the 1,3,3-trimethylindanyl cation which was formed quantitatively by intramolecular electrophilic substitution (eq 1). The lifetime of the acyclic cation was so short that it could not be observed. One expects that a phenyl group should stabilize an allylic cation. However, the availability of intramolecular cyclization as a reaction path causes the acyclic cation to be "chemically unstable." Contributing to this chemical instability is the easy equilibration between conformations a and b which are both expected to be rotated significantly out-of-plane[7] due to the 1,3 methyl or 1,3 methyl–phenyl nonbonded repulsions.



(1)

Conformer b should undergo ready cyclization, and



(2)

a b

one might then expect that phenyl-substituted acyclic allylic cations would only be observable at low temperatures.

A few indanyl cations have been generated by protonating indenes in strong acids.[8,9] The 1-methylindanyl cation underwent complete exchange of the C-2 hydrogens in less than 1 min at 25° in concentrated D_2SO_4.[8] Thus, indanyl cations are in equilibrium with the corresponding indene, but the position of equilibrium greatly favors the cation.

In this paper, we report the first observations of acyclic phenyl-substituted allylic cations. Also, the stereoselective protonation of transient indenes, formed by cyclization of phenyl-substituted allylic cations, is reported. Furthermore, the temperature-dependent hydride shifts of several indanyl cations were observed.

A series of phenyl-substituted allylic cations was

(1) This work is a portion of the Ph.D. Thesis of W. G. M., University of Alabama, University, Ala., 1971. The authors would like to acknowledge Mr. William Jones, an undergraduate research participant, for extensive assistance in the experimental work and to the College Work Study Program for the support of his contributions.

(2) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodges, J. J. Houser, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **85**, 2991 (1963).

(3) (a) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *ibid.*, **87**, 2997 (1965); (b) G. A. Olah and M. B. Comisarow, *ibid.*, **86**, 5682 (1964); (c) G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 6083 (1968).

(4) N. C. Deno and R. R. Lastomirsky, *ibid.*, **90**, 4085 (1968).

(5) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *ibid.*, **91**, 5174 (1969).

(6) C. U. Pittman, Jr., *Chem. Commun.*, 122 (1969).

(7) See, for example, a review by N. C. Deno, "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1970, Chapter 18, p 789.

(8) (a) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 2153 (1965); (b) C. U. Pittman, Jr., Ph.D. Thesis, Pennsylvania State University, University Park, Pa., 1964.

(9) V. Bertoli and P. H. Plesch, *Spectrochim. Acta, Part A*, **25**, 447 (1969).

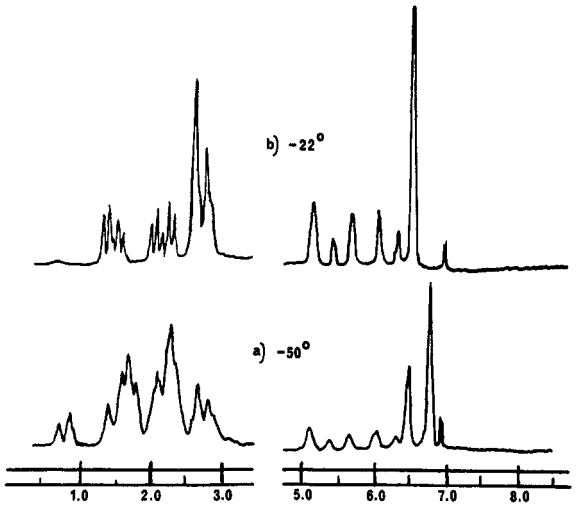


Figure 1. Pmr spectra of (a) an FSO_3H–SO_2 solution of predominately the 1,3-diphenylbutenyl cation (**2a**) in the process of cyclizing to the 1-methyl-3-phenylindanyl cation (**4a**); (b) the resulting 1-methyl-3-phenylindanyl cation at −22°.

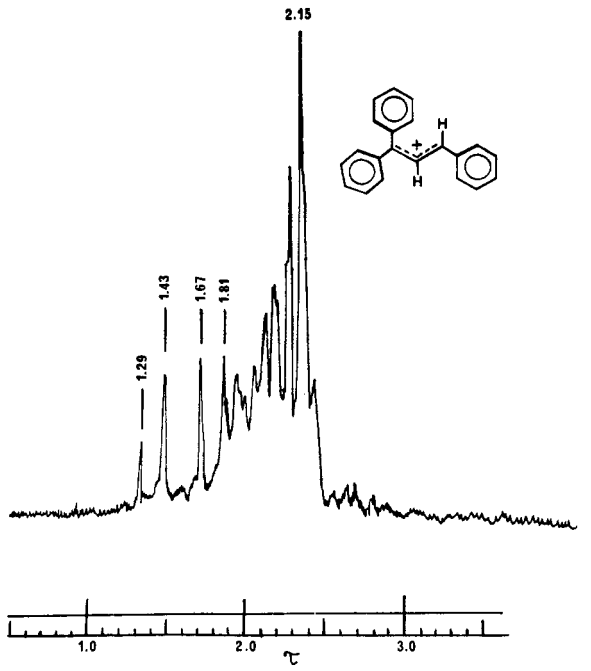


Figure 2. Nmr spectrum of the 1,1,3-triphenylpropenyl cation (**2b**) in FSO_3H–SO_2 at −50°.

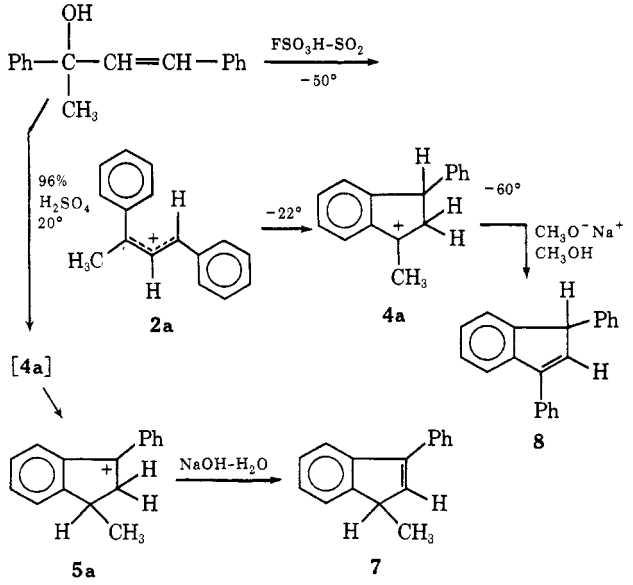
generated from allylic alcohols, and one diene, in the strongly acidic media (FSO_3H–SO_2). The primary mode of investigation was pmr spectroscopy, but deuterium labeling, deuterium exchange studies, and product analysis were also employed. All the allylic cations studied eventually cyclized to indanyl cations. These reactions fall into two categories: (1) cyclization to give an initial indanyl cation which does not rearrange further, and (2) cyclization to give an initial indanyl cation which rearranges to give a more stable indanyl cation (Scheme II). In those cases where subsequent rearrangement follows, variable-temperature pmr studies permitted the cyclization mechanism to be followed stepwise by observing each intermediate ion as the temperature was raised.

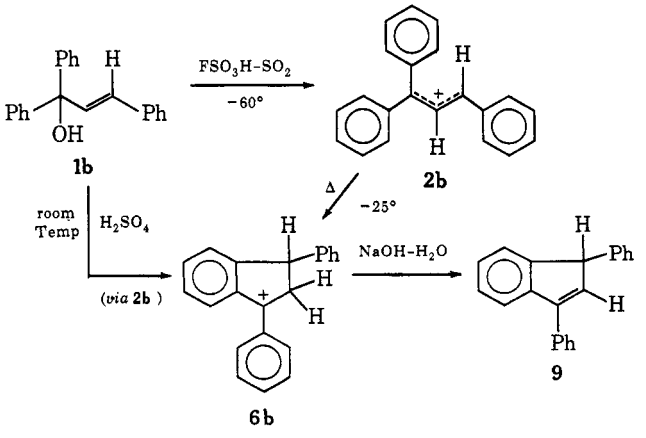
Results

When 2,4-diphenyl-3-buten-2-ol (**1a**) was dissolved into FSO_3H–SO_2, at temperatures from −75 to −50°, the 1,3-diphenylbutenyl cation (**2a**) was generated and observed by pmr (see Scheme I). At −50° the pmr spectra of these solutions show the acyclic cation **2a** in the process of cyclizing to the 1-methyl-3-phenylindanyl cation (**4a**) (see Figure 1). At −70° almost pure solutions of **2a** are obtained. Acyclic ion **2a** readily cyclizes on warming, and at −22° only the cyclic indanyl cation **4a** is observed.[10] However, when alcohol **1a** was added to 96% H_2SO_4 neither **2a** nor **4a** was observed. Instead, the 3-methyl-1-phenylindanyl cation (**5a**) was quantitatively formed.[10] Thus, in both FSO_3H–SO_2 and H_2SO_4, **1a** dehydrates to give the acyclic cation **2a** which cyclizes to produce indanyl cation **4a**. However, in sulfuric acid at room temperature the reaction sequence proceeds farther. Cation **4a** rearranges to give the more stable cation **5a** where two phenyl groups are now in conjugation with charged carbon.

Upon quenching the sulfuric acid solution of **5a** into cold, aqueous sodium hydroxide, 3-methyl-1-phenylindene (**7**) was isolated in 87% yield. Similarly, careful

Scheme I





(10) These cyclizations are quantitative. No other decomposition, alkylation, or other products could be detected. In the strongly acidic FSO_3H–SO_2 or H_2SO_4 media, the concentrations of diene corresponding to **1a** or the indenes corresponding to **4a** or **5a** are so low that second-order alkylation reactions are not observed.

Table I. Pmr (100 MHz) Parameters for Phenyl-Substituted Allylic and Indanyl Cations[a,b]

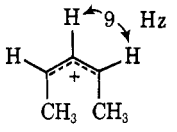
Ion	R_1	R_2	R_3	R_4	H′
2a −50°	Me, 6.74, s	H (coupled to R_4 = H) 0.83 and 0.69 low-field members, J_{AB} = 14 1.37 (calcd)[c]		H (coupled to R_2 = H) 0.77 (calcd)[c]	
2b −50°		H (coupled to R_4 = H) 1.81, 1.67, 1.43, and 1.29, J_{AB} = 14 1.73 (calcd)[c]		H (coupled to R_2 = H) 1.37 (calcd)[c]	
4a −22°	Me, 6.45, s	H (coupled to H′) 6.28, 6.02, 5.62, and 5.36, J_{AB} = 26	Ph, 2.75, m	H, 5.07, s	(see R_2)
4c −40°	Me, 6.47, s	Me, 8.31	Ph, 2.65, m	H, 5.55, s	6.18, q J = 7
4d (cis) −70°	Me, 6.65, s	Ph 3.13, m	Ph, 2.93, m	H, ~4.66	4.66
4d (trans) −70°	Me, 6.75, s	Ph, 2.74, m	Ph, 2.93, m	H, 5.17, s	5.10, s
5a RT[d]	H (coupled to H′) 5.98, 5.74, 5.32, and 5.08, J_{AB} = 24		Me, 8.01, d J = 7	H, ~5.74	(see R_2)
5c (trans) −10°		Me, 8.28, t J = 7	Me, 8.30, t J = 7	H, 6.46, q J = 7	5.89, q J = 7
RT		Me, 7.97, t J = 7	Me, 7.97, t J = 7	H, 5.16, q J = 7	5.89, q J = 7
5d (cis) −30°		Ph, 2.76, m	Me, 8.91, d J = 7	H, 5.92, m	4.35, d J = 4
5d (trans) −30°		Ph, 2.76, m	Me, 8.34, d J = 7	H, 6.28, q J = 7	4.99, s
6b RT		H (coupled to H′) 5.93, 5.59, 5.21, and 4.97, J_{AB} = 24	Ph, 2.41, m	H, 4.77, s	(see R_2)
6e −40°	Me, 6.54, s		Me, 8.44, d J = 7		
6f −15°	Me, 6.42, s	R_2 = R_3 = Me are contained in a multiplet centered at 8.13		H, 6.4	5.95, m
6g −10°	Me, 6.65, s	R_2 = R_3 = R_4 = Me are all contained in a large multiplet centered at 8.53			~6.51
6h −40°	Me, 6.69, s	Ph, 2.57, m	Me, 8.40, s (cis to R_2)	Me, 9.00, s (trans to R_2)	5.28, m, s
6i RT	Me, 6.14, s	H, 5.50, s (coincident with H′)	Me, 7.70, s	Ph, 2.39, m	5.50
6j (cis) −30°		Me, 8.81, d J = 7	Ph, 2.65, m	H, 4.83, d J = 4	5.17, m
6j (trans) −30°		Me, 8.29, d J = 7	Ph, 2.65, m	H, 5.45, s	5.57, q J = 7
6k (cis) −10°		Me, 8.98, d J = 7	Me, 8.04, s		5.55
6k (trans) −10°		Me, 8.42, d J = 7	Me, 8.19, s		5.55
6l +10°		H, H′, AB pattern 5.94, 5.58, 5.22, and 4.98, J_{AB} = 24	Ph, 2.44 A_2B_2, q	H, 4.79, s (broadened)	(see R_2)

[a] Chemical shifts in τ from TMS and coupling constants in Hz; s = singlet, d = doublet, t = triplet, and q = quartet. [b] All data for temperatures below room temperature were obtained with FSO_3H–SO_2, and all room-temperature data were obtained with 96% H_2SO_4. [c] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 199. [d] RT = room temperature.

quenching of a FSO_3H–SO_2 solution of **4a** into sodium methoxide–methanol at ~−60° produced 1-methyl-3-phenylindene (**8**) in 71% yield.

The acyclic 1,1,3-triphenyl-2-propenyl cation (**2b**) was the other acyclic cation to be directly observed. It was formed from 1,1,3-triphenyl-2-propenol (**1b**) in FSO_3H–SO_2 at −60°, but above −30° cyclization occurred. The pmr spectrum of **2b** is shown in Figure 2. At room temperature in H_2SO_4 the 1,3-diphenylindanyl cation (**6b**) was generated directly from **1b** without observation of the open ion **2b**, and upon quenching this solution of 1,3-diphenylindene (**9**) was isolated in 84% yield (see eq 2). Cations **2a** and **2b** are the first acyclic phenyl-substituted allylic cations to be observed, and they are only detected at low temperatures. Their pmr spectra are summarized in Table I. A common characteristic of the pmr spectra of both **2a** and **2b** is the clean AB pattern exhibited by the terminal and central protons on the allylic backbone. The large, 14 Hz, coupling of this pattern indicates these ions possess a fixed, trans, and reasonably coplanar relation to one another. This conclusion is strongly supported by examining aliphatic acyclic allylic cations. Schleyer, *et al.*,[11] reported a 9-Hz coupling in the *cis,cis*-1,3-dimethylallyl cation (**10**), while the *trans,trans*-1,3-dimethylallyl cation (**11**) exhibited a 14-Hz coupling.

(11) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, 91, 5174 (1969).



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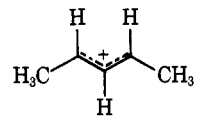

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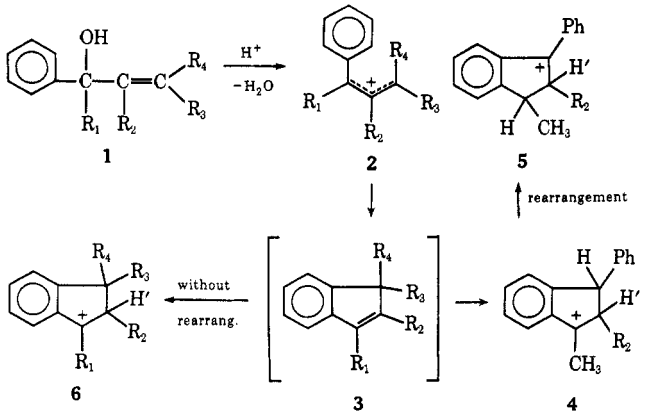
A total of 11 phenyl-substituted allylic alcohols (**1a–l**) were prepared and their reactions studied in strongly acid media (summarized in Scheme II). The acyclic

Scheme II



1 2 5 6 3 4

1, 2, 3, 4, 6

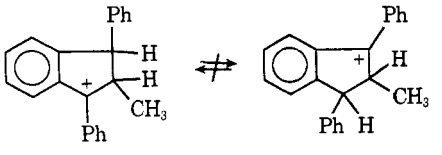
a, R_1 = Me; $R_2 = R_4$ = H; R_3 = Ph
b, $R_1 = R_3$ = Ph; $R_2 = R_4$ = H
c, $R_1 = R_2$ = Me; R_3 = Ph; R_4 = H
d, R_1 = Me, $R_2 = R_3$ = Ph; R_4 = H
e, $R_1 = R_3$ = Me; $R_2 = R_4$ = H
f, $R_1 = R_2 = R_3$ = Me; R_4 = H
g, $R_1 = R_2 = R_3 = R_4$ = Me
h, $R_1 = R_3 = R_4$ = Me; R_2 = Ph
i, $R_1 = R_3$ = Me; R_2 = H; R_4 = Ph
j, $R_1 = R_3$ = Ph; R_2 = Me; R_4 = H
k, $R_1 = R_4$ = Me; $R_2 = R_3$ = Ph
l, R_1 = Ph; $R_2 = R_4$ = H; R_3 = *p*-tolyl

4, 5

a, R_1 = Me; $R_2 = R_4$ = H; R_3 = Ph
c, $R_1 = R_2$ = Me; R_3 = Ph; R_4 = H
d, R_1 = Me; $R_2 = R_3$ = Ph; R_4 = H

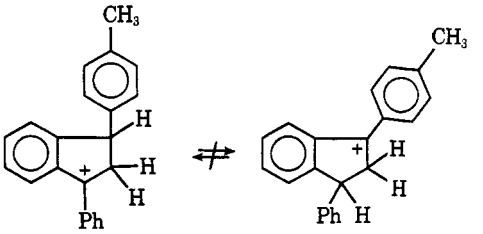
allylic cations **2c–l** were not observed even in the −60 to −70° temperature range. Instead they rapidly cyclized to give indanyl cations. One group, alcohols **1b,e–l**, cyclizes *via* open cations **2b,e–l** to produce unrearranged indanyl cations **2b,e–l**. The second group of alcohols, **1a,c,d**, initially cyclizes *via* open cations **2a,c,d** to indanyl cations **4a,c,d**. However, these cations undergo further rearrangement to ions **5a,c,d**. The three indanyl cations which further rearrange (**4a,c,d**) all possess a methyl group at C-1 and both a phenyl and a hydrogen at C-3. Furthermore, all rearrangements proceed from a 1-methyl- to a 1-phenylindanyl cation.

No further rearrangement takes place whenever an indanyl cation is initially formed with R_1 = Ph (for example, see **6b,j,l**). This is most clearly illustrated in two cases. First, the cyclization of **2j** produces the 1,3-diphenyl-2-methylindanyl cation (**6j**) quantitatively in



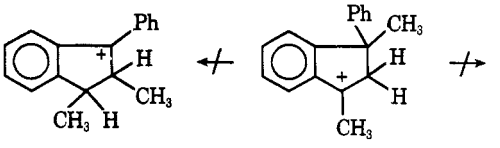
6j

both H_2SO_4 at 25° and FSO_3H–SO_2 at −20 to −70°. If a rearrangement was taking place it would be degenerate, and if the rate were sufficiently fast, both the C-1 and C-3 phenyl groups would equilibrate on the nmr time scale. Even at +50° this was not observed. In the second case, the 1-phenyl-3-*p*-tolylindanyl cation (**6l**) (quantitatively formed from **2l** in FSO_3H at 10°

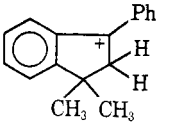


6l

or H_2SO_4 at 25°) does not undergo rearrangement to the 1-*p*-tolyl-3-phenylindanyl cation at room temperature in H_2SO_4. This is significant since the latter would be more stable than **6l**. Finally, it should be mentioned that the 1,3-dimethyl-3-phenylindanyl cation (**6i**) was not observed to rearrange to either the 1-phenyl-3,3-dimethyl- or the 1-phenyl-2,3-dimethylindanyl cations (eq 3).



6i



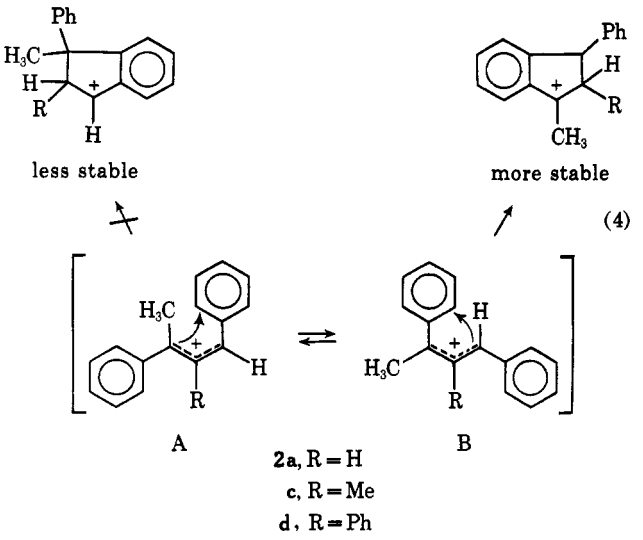
(3)

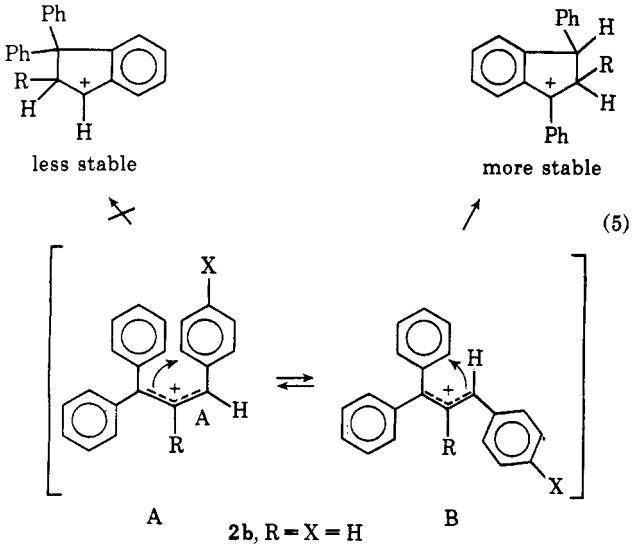
A common feature observed for all the cyclization reactions where a phenyl is present at both ends of the allylic system is the preference for the end of the allylic cation which is least stabilized to effect electrophilic attack. In this circumstance the more thermodynamically stable indanyl cation, of the two that are initially possible, is formed as the kinetic product.[12] Equations 4 and 5 summarize the examples which illustrate this distinction. Note that neither conformation A nor B in eq 4 is the most stable one, but they equilibrate through it.

The observed path could result from (1) a higher concentration of conformer B, (2) an intrinsically greater rate constant for electrophilic attack in conformer B where the less stabilized end of the allylic system attacks the ring, or (3) a combination of both (1) and (2).

Quenching sulfuric acid solutions of the indanyl cations formed above into cold aqueous sodium hydroxide provides a general indene synthesis. The indenes corresponding to the stable indanyl cation end product in the acid (structures **5** and **6**, Scheme II) were isolated in yields of 57 to 97%, with an average yield of 85%.

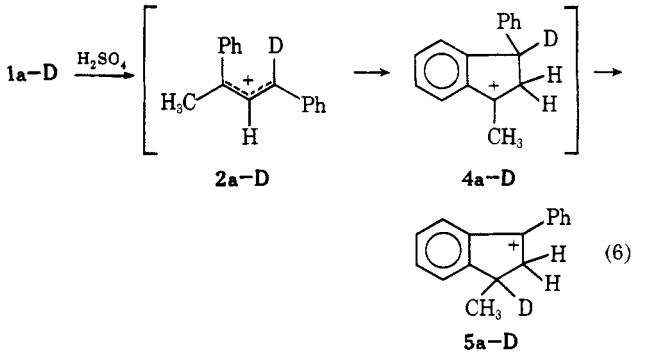
(12) Prior reversible formation of the less stable indanyl cation appears to be ruled out by several observations. For example, the protonation of several indenes, with a hydrogen at C-1, did not give either their corresponding open allylic cations or the observed indanyl cation cyclization products of the corresponding open allylic cations. For example, protonation of 3-methyl-3-phenylindene did not give either **2a** or **4a** under any of the conditions studied (FSO_3H–SO_2 from −70 to +20° or H_2SO_4 at room temperature). Similarly, protonation of 2-methyl-3,3-diphenylindene gave neither **2j** nor **6j**. Furthermore, indanyl cations with hydrogen at C-1 gave dimeric and polymeric products rapidly in FSO_3H–SO_2 at −50°.



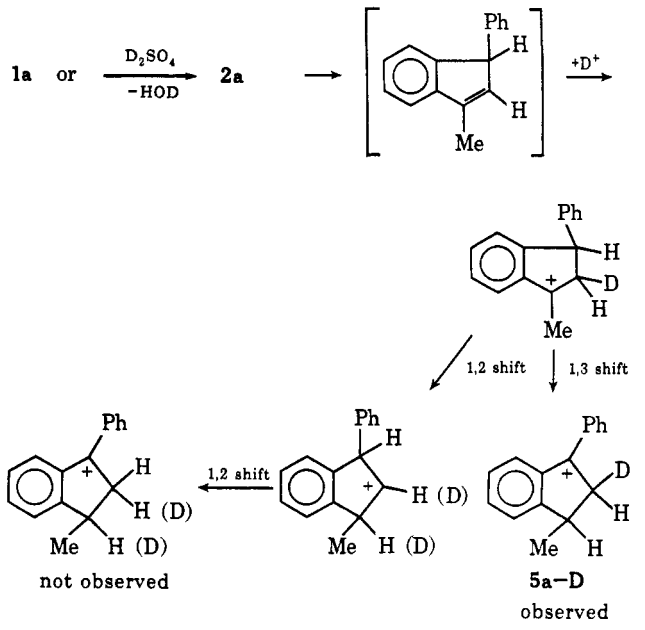


Furthermore, the low-temperature (−70°) quenching of FSO_3H–SO_2 solutions of intermediate indanyl cations **4a–c** into sodium methoxide–methanol resulted in the isolation of the corresponding indenes in yields between 48 and 71%.[13]

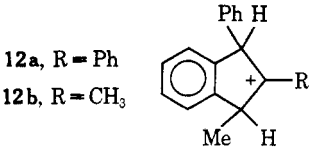
Mechanism of the 4a,c,d → 5a,c,d Rearrangements. The rearrangements of **4a,c,d** to **5a,c,d** can be envisioned as taking place *via* a single 1,3-hydride shift or by two successive 1,2-hydride shifts.[14] The rearrangements of **4a** and **4d** to **5a** and **5d**, respectively, took place by single 1,3 shifts. Conversely, the rearrangement of **4c** to **5c** occurs *via* two successive 1,2-hydride shifts. These conclusions were demonstrated by deuterium labeling and exchange studies. For example, 2,4-diphenyl-3-buten-2-ol-*4*-d_1 (**1a-D**), 90%, was prepared and quantitatively converted, in H_2SO_4 at room temperature, to the 3-methyl-1-phenylindanyl-*3*-d_1 cation (**5a-D**). The pmr spectra of cation **5a-D** exhibited a sharp singlet for its C-3 methyl group and showed no deuterium at C-2. Exclusive formation of **5a-D** rules out a mechanism involving two successive 1,2-hydride shifts, since such a mechanism would predict replacing at least 50% of the C-2 protons by deuterium and incorporating hydrogen at C-3 in **5a-D**. Further support was obtained by generating **5a** from **1a** in 96% D_2SO_4. In this experiment **5a** was deuterated only at C-2. No deuterium was found at C-3 as required by a mechanism involving two consecutive 1,2-hydride shifts (see Scheme III). Similarly, the cyclization of **1d** to



Scheme III



give **5d** in 96% D_2SO_4 did not result in any deuterium incorporation at C-3, and this confirms the 1,3-hydride shift. This is particularly interesting since successive 1,2-hydride shifts would seem favored in the **4d** → **5d** rearrangement, as opposed to the **4a** → **5a** case, due to the availability of the stable tertiary benzyl cation intermediate **12a**. The uncertainty (due to the



nmr technique both in acid and of the drown products in CCl_4) is estimated at ±2–3%.

The rearrangements of **4a** and **4d** contrast sharply with the **4c** to **5c** rearrangement which does proceed by successive 1,2-hydride shifts. Thus the **4c** to **5c** rearrangement is proceeding through tertiary (but not benzylic) cation **12b**. Generation of **5c** from **1c** in 96% D_2SO_4 or FSO_3D resulted in complete deuteration

(13) The synthesis of indenes from phenyl-substituted allylic alcohols appears general and will be the subject of a subsequent paper.

(14) Intramolecular hydride shifts have been extensively investigated. For a recent review, see G. J. Karabatsos and J. L. Fry, in ref 7, pp 521–572.

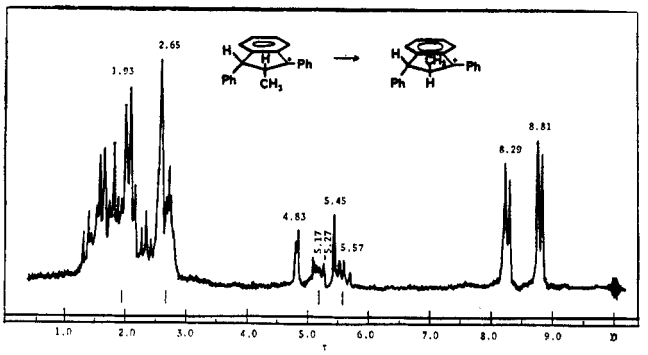
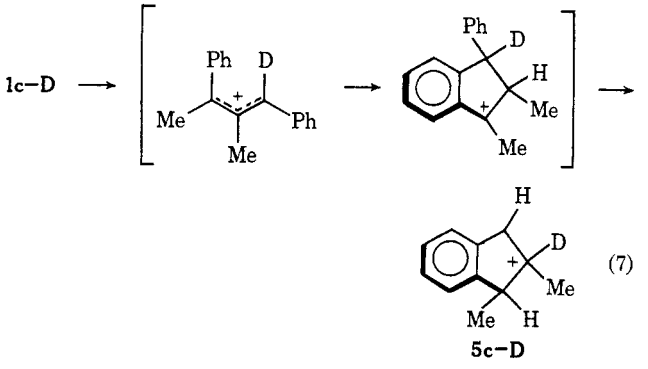


Figure 3. Nmr spectrum showing the *cis*-1,3-diphenyl-2-methylindanyl cation (**6j**) converting to the *trans*-1,3-diphenyl-2-methylindanyl cation (**6j**) in FSO_3H–SO_2 at −30°.

at C-3 but no deuterium incorporation at C-2.[15] These results are only readily explained by a mechanism involving two 1,2-hydride shifts. This was further confirmed by generating **5c-D** from 2,4-diphenyl-3-methyl-3 buten-2-ol-*4*-d_1 (**1c–D**), in FSO_3H–SO_2 at −10°. In this case all the deuterium in **5c-D** was found at C-2 and none was found at C-3 (see eq 7).[16]



(7)

Stereoselective Protonation of Transient Indenes. The cyclizations of phenyl-substituted allylic cations (**2a–l**) to indanyl cations proceed by an intramolecular SEAr mechanism. This requires the formation of an intermediate indene (see **3**, Scheme II) which is subsequently protonated in the acidic media. Several of the transient indenes are capable of stereoselective protonation, and this has now been demonstrated in four examples (**3c,d,j,k**). Two of these cases, **3j** and **3d**, will be discussed in detail.

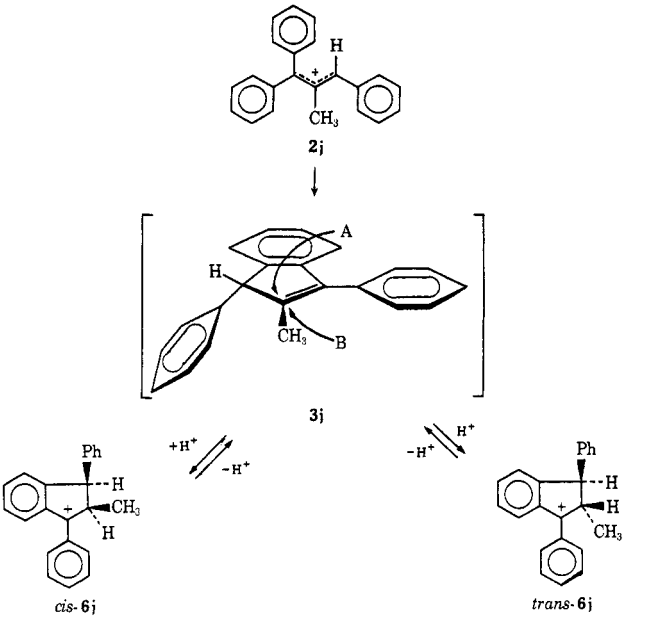
Upon dissolving 3-methyl-2,4-diphenyl-3-buten-2-ol (**1j**) into FSO_3H–SO_2 at −70°, one obtains a solution consisting predominantly (>80%) of the *cis*-1,3-diphenyl-2-methylindanyl cation (**6j**).[17] However, *cis*-**6j** equilibrates readily to the more stable *trans*-**6j** (see Scheme IV). On standing or warming, *trans*-**6j** is progressively formed (at −30° after 0.5 hr about 50% cis and 50% trans were present) until at −15° only *trans*-**6j** remains. On recooling to −70° no further

(15) The pmr spectrum of **5c** generated in D_2SO_4 exhibited a clean singlet for the C-3 methyl group at τ 7.97. When **5c** was generated from **1c** in FSO_3D–SO_2 at −15° the methyl group at C-2 appears as a clean doublet at τ 8.27, J = 7 Hz, and the proton at C-2 as a quartet at τ 5.87, J = 7 Hz.

(16) The C-3 methyl appeared at τ 8.30 and the C-2 methyl group was a singlet τ 8.28. The proton at C-3 appeared at 6.46, q, J = 7.0 Hz, but the C-2 proton at τ 5.89 was gone.

(17) In two such experiments, where special care was taken to precool an SO_2 solution of **1j** before addition to the acid and where the addition was done very slowly with vortex action stirrer, *cis*-**6j** was produced in >90% yield.

Scheme IV



changes occurred. *cis*- and *trans*-**6j** are readily differentiated by pmr since the C-2 methyl group of the cis ion lies in the face of the phenyl ring at C-3. Thus, it is abnormally shielded (sharp doublet at τ 8.81), whereas the C-2 methyl resonance in the trans ion is found at τ 8.29. Moreover, the coupling between protons on C-2 and C-3 is 4 Hz in the case of *cis*-**6j**, but is ~0 Hz in *trans*-**6j**. The magnitudes of these coupling constants are completely in accord with the dihedral angles between these two sets of protons.[18] Thus, stereoselective protonation of **3j** is occurring trans to the C-3 phenyl substituent (path A, Scheme IV) producing the less stable ion, *cis*-**6j**. Clearly, path A is kinetically favored, and this is probably dictated by the fact that this path results in less steric hindrance, from the C-3 phenyl group, to the approach of the proton donor.[19] *trans*-**6j** does not have a cis 1,2 phenyl–methyl eclipsing interaction. Thus, as the temperature is raised, *cis*-**6j** can convert to the more stable thermodynamic product *trans*-**6j** *via* the equilibrium with indene **3j**. The pmr spectrum of a FSO_3H–SO_2 solution of *cis*-**6j** in the process of equilibrating to *trans*-**6j** is shown in Figure 3.

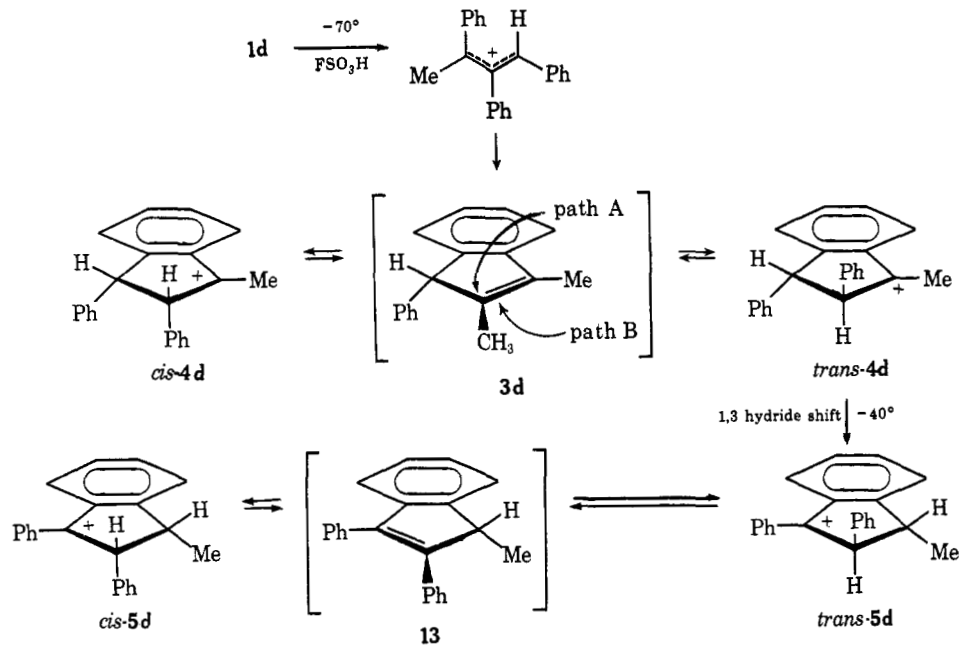
The product obtained when 2,3,4-triphenyl-3-buten-2-ol (**1d**) is dissolved in FSO_3H–SO_2 at −70° is a mixture of the *cis*- and *trans*-2,3-diphenyl-1-methylindanyl cations (**4d**). Depending upon the care taken in the preparation of these solutions, the cis isomer predominates from 90 to >65%.[20] Even at −70° *cis*-**4d** is completely converted to *trans*-**4d** in 70 min

(18) For a summary of vicinal coupling constants in ring systems, see L. M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, Chapters 4-2 and 4-3.

(19) The proton donor is presumably the FSO_3H molecule which has considerable steric bulk. If the transition state for the protonation of indenes closely resembles the cation being formed, it seems likely that the bulk of the FSO_3H molecule, with its solvent shell, would make itself felt in a competition between paths A and B. Stereospecific protonation of cyclopentadienes has been reported by T. S. Sorensen, I. J. Miller, and C. M. Urness, *Can. J. Chem.*, **48**, 3374 (1970).

(20) In most experiments a very small, constant concentration of the *cis*-1,2-diphenyl-3-methylindanyl cation (**5d**) was present from the beginning, even at +70°. This is presumably due to hot-spots during the preparation of the solutions. As the temperature increases above −40°, the cis/trans ratio continuously decreases from the initial ratio of ~1 at −40°. When the ratio is ~1, not all the *trans*-**4d** has been consumed.

Scheme V



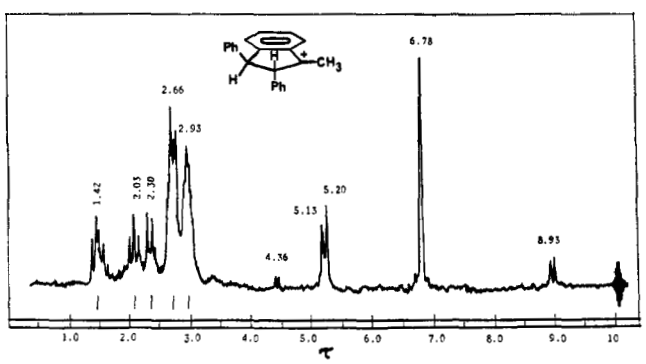


Figure 4. Nmr spectrum of predominately the *trans*-2,3-diphenyl-1-methylindanyl cation (**4d**), with a trace of the *cis*-1,2-diphenyl-3-methylindanyl cation (**5d**) present in FSO_3H–SO_2 at −50°.

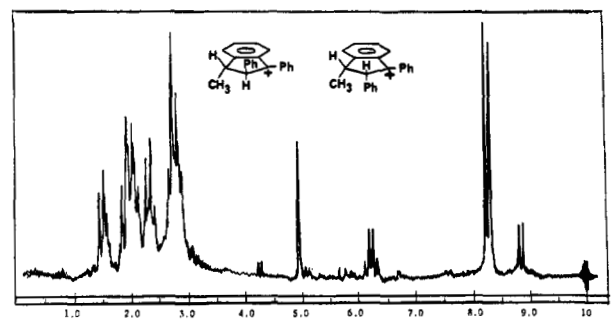


Figure 5. Nmr spectrum showing predominately the *trans*-1,2-diphenyl-3-methylindanyl cation (**5d**), along with a smaller concentration of the *cis*-1,2-diphenyl-3-methylindanyl cation (**5d**) in FSO_3H–SO_2 at −20°.

(see Scheme V). *trans*-**4d** persisted in nearly quantitative amounts as the solution was warmed to −40° (see Figure 4).[20] At −40° the rearrangement of *trans*-**4d** to *trans*-**5d** began to occur. This was the first appearance of *trans*-**5d** in the solution. As the concentration of *trans*-**5d** increased at −40° a slight increase in the concentration of *cis*-**5d** took place.[20] However, *cis*-**5d** never predominated, and the maximum cis/trans **5d** ratio ~1 occurred at −40°. Above −40° the *trans*-**5d** concentration was always greater than that of *cis*-**5d**, and after 15 min at −20° the conversion was nearly complete, with >90% of *trans*-**5d** present (Figure 5 shows pmr spectrum of *trans*-**5d** with a small amount of *cis*-**5d** remaining).

Stereoselective protonation of indene, **3d**, like that of **3j**, more readily takes place from the least hindered face of the five-membered ring (*i.e.*, path A, Scheme V). This leads to an initial dominant concentration of *cid*-**4d** which is the kinetic product in the protonation of indene **3j**. However, kinetic product, *cis*-**4d**, with its serious 1,2 phenyl–phenyl eclipsing interaction is less stable than *trans*-**4d** where this interaction has been relieved. Therefore, even at −70°, *cis*-**4d** is gradually converted to *trans*-**4d**.

At −40° *trans*-**4d** begins to undergo a 1,3-hydride shift to produce *trans*-**5d**. The slightly increased concentration of *cis*-**5d** might originate from *trans*-**5d** *via* indene **13** (or by an obscure path). Note that direct intramolecular rearrangement of *trans*-**4d** to *cis*-**5d** by a 1,3- or two 1,2-hydride shifts is not possible. Elevating the temperature above −30° displaces the observed ratio of *cis*- to *trans*-**5d** resulting in less *cis*-**5d**, and after a few minutes at −20°, greater than 90% *trans*-**5d** was present.

cis- and *trans*-**4d** are distinguished from one another by the presence of two singlets for the methyl groups at C-1 (for *cis*-**4d** at τ 6.65 and *trans*-**4d** at 6.75). In *trans*-**4d** the protons on C-2 and C-3 are uncoupled and appear as two singlets at τ 5.10 and 5.17.[21] Comparing *cis*- and *trans*-**5d**, the C-3 methyl group of *cis*-**5d** is abnormally shielded by the phenyl ring at C-2 and appears as a doublet at τ 8.91, while for *trans*-**5d** the methyl doublet appears at τ 8.34. Also, the couplings between the protons on C-2 and C-3 are 4 Hz for *cis*-**5d**, but ~0 Hz for *trans*-**5d**.

Throughout these studies it was easy to distinguish

(21) Again, the trans vicinal coupling constants are ~0 Hz (see discussion of *cis*- and *trans*-**6j** and ref 17.

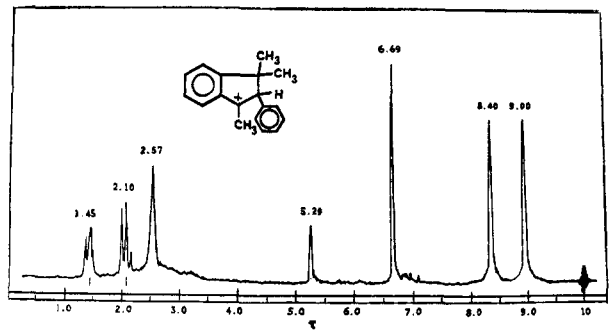
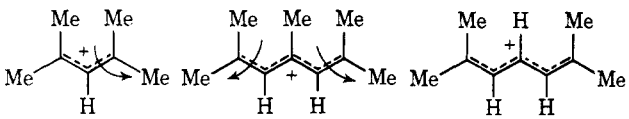


Figure 6. Nmr spectrum of the 1,3,3-trimethyl-2-phenylindanyl cation (**6h**) in FSO_3H–SO_2 at −40°.

between *cis*- and *trans*-indanyl cations. Where a phenyl and methyl are cis, on adjacent carbons, the methyl group is abnormally shielded, and its nmr absorption always occurs at higher fields than in the trans cation. The pmr spectrum of the 2-phenyl-1,3,3-trimethylindanyl cation (**6h**) in FSO_3H–SO_2 at −40° clearly emphasizes this point (see Figure 6). The methyl group at C-3 cis to the phenyl ring at C-2 appears at τ 9.00 while the trans C-3 methyl appears at τ 8.40. Furthermore, when indanyl cations have a single proton at both C-2 and C-3 the vicinal proton cis and trans couplings in all cases are $J_{cis} \simeq 4$ Hz and $J_{trans} \simeq 0$ Hz.

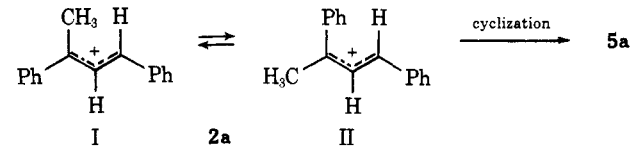
Discussion

Of all the phenyl-substituted allylic cations generated, **2a–l**, only two (**2a** and **2b**) were stable enough to be directly observed by pmr at −70° in FSO_3H. This stability is due to (1) the presence of at least two terminal phenyl substituents and more importantly (2) the lack of serious steric interactions which would cause either **2a** or **2b** to deviate significantly from a coplanar geometry. Studies by Adrain,[22] Deno,[7,23] and Sorensen[24] on both allylic and dienylic cations showed that the planes of the terminal carbons must be rotated far out-of-plane to prevent interpenetration of the van der Waals radii of terminal methyl substituents. For example, in the 2,4-dimethylpentenyl cation (**14**)



14 **15** **16**

this rotation is from 30 to 45°.[7,22,23] Similarly, significant nonplanarity of the 2,4,6-trimethylheptadienyl cation (**15**) accounts for its great cyclization tendency relative to the 2,6-trimethylheptadienylic cation (**16**), which is stable for hours in H_2SO_4 at 25°.[8,24] Out-of-plane rotation reduces the resonance energy, and hence the stability, of the allylic cation involved. As the stability is decreased (relative to the energy of the transition state for rotation), the rotational barrier is decreased and rotation into conformations which are favorable to cyclization readily occur. For example, **2a** can exist in conformations I and II but only II can cyclize. However, the stability of the cation itself is of primary importance in cyclization as **2b** illustrates. This ion always exists in a conformation favorable to cyclization; yet it was observed. When the terminal H of **2a**



I **2a** II

is replaced by methyl or phenyl groups, then there is no conformation where coplanarity of the terminal carbons is permitted and these cations all cyclize rapidly. In fact, replacing the C-3 proton with either a methyl or phenyl has the same effect. Only in **2a** and **2b** are both 1,3 and 1,2 steric interactions absent.

The observed hydride shifts must take place by a suprafacial route. The fact that such shifts are confined to one face of the five-membered ring leads to an important stereochemical consequence. A *cis*-indanyl cation must rearrange to give a new cis cation and a *trans*-indanyl cation rearranges only to a new trans cation. This occurs whether two 1,2-hydride shifts or only a single 1,3-hydride shift is involved.

The reason why **4a** and **4d** rearrange by a single 1,3-hydride shift while **4c** rearranges by means of two 1,2-hydride shifts is not clear. Certainly a 1,3 shift would be favored in **4a** because an unstable secondary carbonium ion intermediate would be necessary if two 1,2 shifts occurred. In **4d**, however, consecutive 1,2 shifts would proceed through a stable tertiary benzylic intermediate (**12a**). Since **4d** does, in fact, rearrange by a single 1,3 shift, this suggests that other factors inherently favor the 1,3 shift in indanyl cations. However, the fact that **4c** rearranges by two 1,2 shifts leads to the opposite conclusion. One can suggest that the phenyl ring at C-2 does not easily achieve coplanarity with C-2 in intermediate cation **12a**. Thus, **12a** might not enjoy benzylic conjugation stabilization[25] and this would promote a mechanism involving a 1,3 shift.

Experimental Section

Preparation of Ions. The FSO_3H–SO_2 cation solutions used for low-temperature work were prepared in the following manner. The appropriate precursor (0.5 g) was dissolved in liquid SO_2 (1.0 ml) and the solution lowered to Dry Ice–acetone temperature. This solution was then slowly added to FSO_3H (1.0 ml), precooled to the same temperature, with the use of vigorous stirring. A portion of the final solution was added to a pmr tube cooled to the same temperature, and the pmr tube transferred from its Dry Ice–acetone bath to the spectrometer.

The H_2SO_4–cation solutions used at room temperature were prepared by dissolving the precursor (0.5 g) in a few milliliters of CCl_4 (quantity depending on the solubility), and this solution slowly added to a rapidly stirring mixture of H_2SO_4 (1.0 ml) and CCl_4 (~3 ml) cooled in an ice–water bath. A portion of the final solution was then transferred to a pmr tube, a TMS capillary was inserted, and the spectra were obtained.

Pmr Spectra. A Varian Model HA-100 spectrometer equipped with a variable-temperature probe, and using a TMS capillary as reference, was used for all spectra.

All the cations reported were identified by their pmr spectra, and these are summarized in Table I. Aryl protons at the C-4, -5, -6, and -7 positions of all the indanyl cations appear between τ 1.0 to 2.5 in both FSO_3H–SO_2 and H_2SO_4. Protons on phenyl rings bonded to C-1 (in conjugation with the charge) also appear within this region, and consequently in the 1-phenylindanyl

(22) F. J. Adrain, *J. Chem. Phys.*, **28**, 608 (1958).
(23) N. C. Deno, R. C. Haddon, and E. N. Norwak, *J. Amer. Chem. Soc.*, **92**, 6691 (1970).
(24) For a summary, see T. Sorensen in ref 7, pp 807–836.
(25) However, studies with models do not show any strong steric interactions which would prevent planarity.

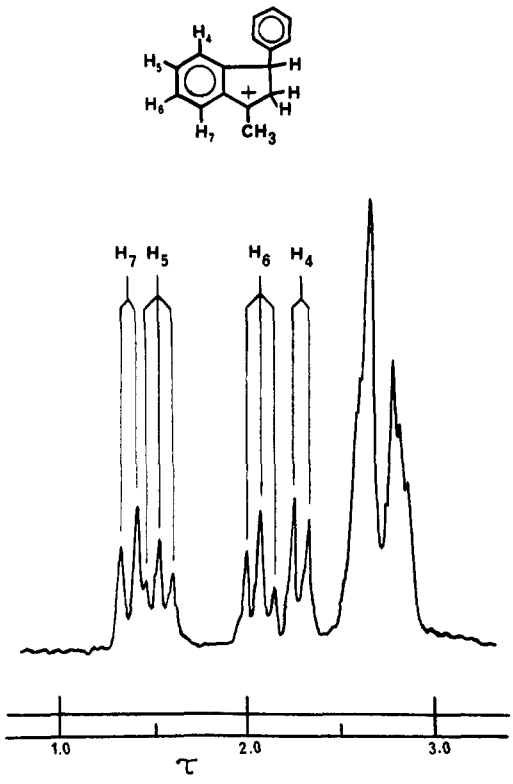


Figure 7. Detail from the nmr spectrum of the 2-phenyl-1,3,3-trimethylindanyl cation (**6h**) in FSO_3H–SO_2 at −40°.

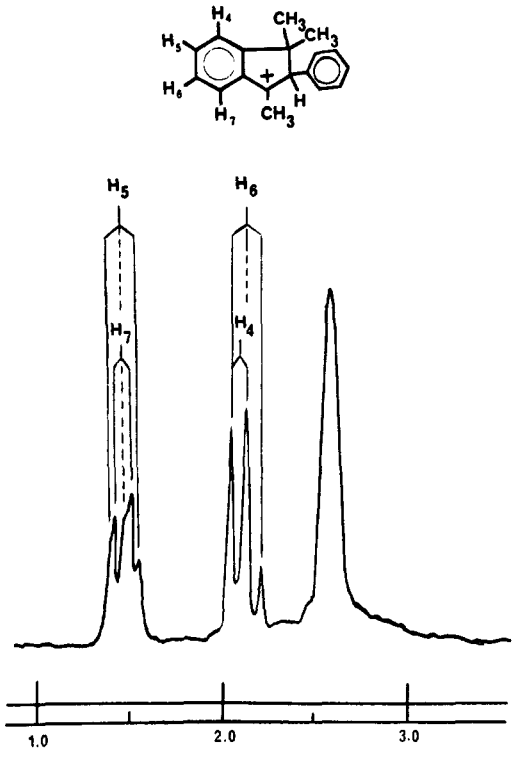


Figure 8. Detail from the nmr spectrum of the 1-methyl-3-phenylindanyl cation (**4a**) in FSO_3H–SO_2 at −22°.

cations it is difficult to completely differentiate and accurately assign the multiplets in this region. For brevity they are not included in Table I. Protons on phenyl groups bonded to C-2 and C-3 appear sufficiently upfield and are readily distinguished from aromatic protons where the phenyl group is conjugated to the charge center. In indanyl cations which do not have a C-1 phenyl group, the protons at C-4, -5, -6 and -7 appear as two or three multiplets. The pmr spectra of ions **6h** (Figure 7) and **4a** (Figure 8) illustrate this point. Greater delocalization of charge to C-5 and -7 occurs. Consequently, the C-5 and C-7 protons are deshielded more than those at C-4 and C-6 by τ 0.3–0.5 in all cases studied.[26] The C-5 and C-7 protons appear as a single overlapping multiplet. The C-4 and C-6 protons occur as either one multiplet (**6h**, Figure 7) or in some cases (**4a**, Figure 8), where the C-4 protons sufficiently upfield from the C-6 proton, they appear as a resolved doublet and triplet, respectively, with J = 8 Hz in both cases. Throughout this study, spectra of high quality were obtained as exemplified in those shown in the figures.

Materials. 2,4-Diphenyl-3-buten-2-ol (1a) was prepared by the addition of methyllithium (0.15 mol) to benzalacetophenone (31.7 g, 0.15 mol) in ether. The mixture was refluxed for 30 min, cooled, and hydrolyzed with aqueous ammonium chloride. The ether solution was dried ($MgSO_4$) and concentrated to give a yellowish oil which crystallized. The crude product was recrystallized twice from *n*-hexane to give 30 g (88%) of 2,4-diphenyl-3-buten-2-ol: mp 58–59°; pmr (CCl_4) τ 8.40 (s, 3 H, PhCCH_3), 7.18 (s, 1 H, OH), 3.64 (AB pattern J = 8 Hz, $-CH_A{=}CH_B-$), and 2.78 (m, 10 H, phenyl CH).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19; O, 7.13. Found: C, 85.85; H, 7.28; O, 6.87.

1,1,3-Triphenyl-2-propenol (1b) was prepared according to the method of Luttringhaus,[27] having mp 110–112° and exhibiting the expected ir and nmr spectra.

2,4-Diphenyl-3-methyl-3-buten-2-ol (1c) was prepared by the addition of methyllithium (0.20 mol) to benzalpropiophenone[28] (40.1 g, 0.18 mol) in ether. The mixture was refluxed for 30 min, cooled, and hydrolyzed with aqueous ammonium chloride. The ether solution was dried (K_2CO_3), concentrated, and vacuum distilled to give 33.2 g (77%) of 2,4-diphenyl-3-methyl-3-buten-2-ol: bp 127–130° (0.22 mm); n^{22}D 1.5956; pmr (CCl_4) τ 8.40 (s, 3 H, PhCCH_3), 8.37 (s, 3 H, $=CCH_3$), 7.34 (s, 1 H, OH), 3.25 (s, 1 H, PhCH=), and 2.85 (m, 10 H, phenyl CH).

Anal. Calcd for $C_{17}H_{18}O$; C, 85.69; H, 7.60; O, 6.71. Found: C, 85.65; H, 7.76; O, 6.63.

2,3,4-Triphenyl-3-buten-2-ol (1d) was prepared by the addition of methyllithium (0.07 mol) to 1,2,3-triphenyl-2-propenone[29] (20.3 g, 0.07 mol) in ether. The mixture was refluxed for 2.5 hr, cooled, and hydrolyzed with aqueous ammonium chloride. The ether solution was dried (K_2CO_3) and concentrated to give an oily residue that slowly crystallized. The solid was recrystallized from *n*-hexane to give 14.5 g (68%) of 2,3,4-triphenyl-3-buten-2-ol: mp 83–84°; pmr (CCl_4) τ 8.32 (s, 3 H, PhCCH_3), 8.04 (s, 1 H, OH), and 3.04 (m, 16 H, =CH and phenyl CH).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.95; H, 6.72; O, 5.33. Found: C, 87.82; H, 6.97; O, 5.21.

2-Phenyl-3-penten-2-ol (1e) was prepared according to the method of Levy and Normant[30] having bp 54–55° (0.1 mm) and exhibiting the expected ir and nmr spectra.

3-Methyl-2-phenyl-3-penten-2-ol (1f) was prepared by the reaction of 2-butenyl-2-magnesium bromide with acetophenone in tetrahydrofuran. Magnesium turnings (8.89 g, 0.37 mol) and THF (40 ml) were placed in a flask with a trace of iodine; 2-bromo-2-butene (5.0 ml, 6.39 g) was then added. When reaction commenced, stirring was started, and 2-bromo-2-butene (43.3 g, 0.32 mol) in 130 ml of THF was added at such a rate that the temperature was maintained between 40 and 50°. When addition was complete, the mixture was heated at 70–80° for 1 hr, then cooled, and acetophenone (32.8 g, 0.28 mol) in an equal volume of THF added over a 30-min interval. The mixture was then refluxed for 4 hr, cooled, and hydrolyzed with aqueous ammonium chloride. The THF solution was dried (K_2CO_3), concentrated, and vacuum distilled to give 27.5 g (55%) of 3-methyl-2-phenyl-3-penten-2-ol: bp 72–73° (1.8 mm), lit.[31] bp 100° (4 mm); pmr (CCl_4) τ 8.60 (d, 3 H, J = 4 Hz, CH_3CH=), 8.40 (s, 3 H, PhCCH_3), 7.22 (s, 1 H, OH), 4.67 (q, 1 H, J = 4 Hz, CH_3CH=), and 2.76 (m, 5 H, phenyl CH).

(26) In the dimethylphenyl carbonium ion, the ortho and para protons are similarly deshielded relative to meta protons. See, for example, D. G. Farnum, *J. Amer. Chem. Soc.*, **89**, 2970 (1967).
(27) A. Luttringhaus, *Chem. Ber.*, **67**, 1602 (1934).
(28) E. P. Kohler, *Amer. Chem. J.*, **31**, 655 (1904).
(29) E. P. Kohler and E. M. Nygaard, *ibid.*, **52**, 4128 (1930).
(30) V. Levy and H. Normant, *C. R. Acad. Sci.*, **244**, 203 (1957).
(31) V. I. Esafov, *Zh. Obshch. Khim.*, **27**, 2667 (1957).

3,4-Dimethyl-2-phenyl-3-penten-2-ol (1g) was prepared by the reaction of 3-methyl-2-butenyl-2-magnesium bromide with acetophenone, after prior preparation of 2-bromo-3-methyl-2-butene.

2-Methyl-2-butene (205 g, 2.92 mol), dissolved in anhydrous ether, was cooled to −15°, and dry bromine (474 g, 2.97 mol) added slowly in the absence of light. The reaction mixture was warmed to room temperature and the excess bromine destroyed with dilute, aqueous sodium thiosulfate. The ether solution was dried (K_2CO_3) and concentrated and the crude product dehydrobrominated without further purification.

A solution of potassium hydroxide (211 g, 3.76 mol) in 1100 ml of ethanol and 100 ml of water was heated to reflux. The crude 2,3-dibromo-2-methylbutane was added at such a rate that reflux was maintained without external heat. The mixture was then heated for 7 hr, cooled, and vacuum filtered to remove the potassium bromide. This solution was poured into water and the bottom layer removed and dried (K_2CO_3). It was then distilled to give 207 g (48%) of 2-bromo-3-methyl-2-butene: bp 116–122°, lit.[32] 118–120°; pmr (CCl_4) τ 8.28 (s, 3 H, CH_3C=), 8.20 (s, 3 H, CH_3C=), and 7.79 (s, 3 H, CCH_3Br).

Magnesium turnings (10.8 g, 0.44 mol), 2-bromo-3-methyl-2-butene (64.4 g, 0.42 mol), acetophenone (27.6 g, 0.23 mol), and tetrahydrofuran were used to prepare 3,4-dimethyl-2-phenyl-3-penten-2-ol in a similar manner to that given for **1f**. The crude product contained residual acetophenone, ir (neat) 1684 cm^{-1} (C=O), which was removed by extraction in the form of its relatively water soluble oxime derivative. The residue from the extraction procedure was vacuum distilled to give 15.5 g (36%) of 3,4-dimethyl-2-phenyl-3-penten-2-ol: bp 76–78° (0.45 mm); $n^{22}D$ 1.5305; pmr (CCl_4) τ 8.58, 8.50, 8.37, and 8.23 (four 3 H singlets of the methyl groups), 7.46 (s, 1 H, OH), and 2.80 (m, 5 H, phenyl CH).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.53; O, 8.42. Found: C, 81.88; H, 9.60; O, 8.52.

2,3-Diphenyl-4-methyl-3-penten-2-ol (1h) was prepared by the reaction of 2-methyl-1-phenylpropenylmagnesium bromide with acetophenone in tetrahydrofuran after prior preparation of 1-bromo-2-methyl-1-phenylpropene[33] (57.9 g, 0.44 mmol) and bromine (70.3 g, 0.44 mol) in a similar manner to that already described for **1g**. The crude product was vacuum distilled to give 93.9 g (73%) of 1,2-dibromo-2-methyl-1-phenylpropane, bp 150° (20 mm).

The 1,2-dibromo-2-methyl-1-phenylpropane was dehydrobrominated as described for **1g**, using potassium hydroxide (19.8 g, 0.35 mol) in 150 ml of ethanol and 7 ml of water. Vacuum distillation of the crude product gave 47.4 g (73%) of 1-bromo-2-methyl-1-phenylpropane: bp 112–116° (15 mm); pmr (CCl_4) τ 8.43 and 8.17 (two singlets, each 3 H, $=CCH_3$), and 2.87 (s, 5 H, phenyl CH).

Magnesium turnings (2.73 g, 0.11 mol), 1-bromo-2-methyl-1-phenylpropene (23.6 g, 0.11 mol), acetophenone[34] (13.4 g, 0.11 mol), and tetrahydrofuran were employed as previously described to prepare **1h**. Again, residual acetophenone was removed by extraction as the oxime derivative, giving 8.4 g (35%) of 2,3-diphenyl-4-methyl-3-penten-2-ol: bp 136–146° (0.3 mm); pmr (CCl_4) τ 8.75 (s, 3 H, $PhCCH_3$), 8.61 and 8.53 (two singlets, each 3 H, $=C(CH_3)_2$), and 2.70 (m, 10 H, phenyl CH).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.61; H, 7.99; O, 6.34. Found: C, 85.82; H, 8.00; O, 6.18.

2,4-Diphenyl-1,3-pentadiene (1i) was prepared according to the method of Freeman,[35] having bp 125–130° (0.17 mm) and exhibiting the expected ir and nmr spectra.

1,1,3-Triphenyl-2-methyl-2-propenol (1j) was prepared by the addition of methyllithium (0.20 mol) to α-methylcinnamate[36] (17.6 g, 0.10 mol) in ether. The mixture was refluxed for 1.5 hr, then stirred at room temperature for 2 hr, and hydrolyzed with aqueous ammonium chloride. The ether solution was dried (K_2CO_3), concentrated, and vacuum distilled with one major fraction collected at 183° (0.1 mm). The distillate crystallized on cooling to give 25.6 g (85%) of 1,1,3-triphenyl-2-methyl-2-propenol: mp 122–122.5°; pmr (CCl_4) τ 8.20 (s, 3 H, $=CCH_3$), 7.63 (s, 1 H, OH), 3.77 (s, 1 H, $PhCH$=), and 2.78 (m, 15 H, phenyl CH).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71; O, 5.33. Found: C, 87.77; H, 6.91; O, 5.32.

2,4,4-Triphenyl-3-penten-2-ol (1k) was prepared by the reaction of 1,1-diphenylpropenyl-2-magnesium bromide with acetophenone. Prior preparation of 2-bromo-1,1-diphenylpropene was carried out by the method described for 2-bromo-3-methyl-2-butene under **1g**.

1,1-Diphenylpropene[37] (43.9 g, 0.23 mol) and dry bromine (38.1 g, 0.24 mol) were used to prepare 1,2-dibromo-1,1-diphenylpropane. The crude, oily dibromide product was dehydrobrominated using a solution of potassium hydroxide (14.0 g, 0.25 mol) in 130 ml of ethanol and 13 ml of water. Vacuum distillation of the crude product gave 34.0 g (55%) of 2-bromo-1,1-diphenylpropene: bp 131–133° (0.3 mm); pmr (CCl_4) τ 7.66 (s, 3 H, $=CCH_3$) and 2.90 (m, 10 H, phenyl CH).

Magnesium turnings (3.21 g, 0.13 mol), 2-bromo-1,1-diphenylpropene (36.1 g, 0.13 mol), acetophenone (10.6 g, 0.09 mol), and tetrahydrofuran were used to carry out the Grignard reaction as in previous reactions described above. The crude product was column chromatographed on silica gel (30–70 mesh) using benzene. 1,1-Diphenylpropene (20.1 g, 0.02 mol) was recovered along with 7.08 g (26%) of nearly pure 2,4,4-triphenyl-3-methyl-3-buten-2-ol: pmr (CCl_4) τ 8.33 (s, 3 H, $PhCCH_3$), 8.21 (s, 3 H, $=CCH_3$), 7.94 (s, 1 H, OH), 7.41 (s, impurity less than 1 H), 5.04 (m, impurity less than 1 H), and 2.86 (m, 17 H, phenyl CH). Infrared bands (neat) at 1646 and 1562 (C=C diene) and 910 cm^{-1} ($=CH_2$) confirmed that the contaminate was 1,1,3-triphenyl-2-methyl-1,3-butadiene from some dehydration of **1k**. Since the alcohol or diene could be used interchangeably in the carbonium ion generation step, no further purification was required.

1,1-Diphenyl-3-*p*-tolyl-2-propen-1-ol (1l) was prepared by reacting phenylmagnesium bromide (0.1 mol) with 1-phenyl-3-*p*-tolyl-2-propenone[38] (20 g, 0.09 mol) in diethyl ether at 36° for 10 hr. The crude product was purified by removing the unreacted ketone as its oxime and chromatographing the alcohol through a 1-ft long, 1.5-in. diameter column of silica gel with chloroform. The alcohol appeared pure at this stage: pmr (CCl_4) τ 3.42 (AB pattern, 2 H, J = 8 Hz, $-CH$=$CH-$), 2.81 (m, 10 H, phenyl protons), 2.86 (A_2B_2 pattern, partly obscured by phenyl protons, 4 H, phenyl protons), 2.44 (s, 3 H, *p*-CH_3); ir (KBr) 3530 (OH), 986, and 905 (vinyl H). It was used without further purification.

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