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1-Phenylallyl Cations and Their Rearrangement to Indanyl Cations in Superacidic Media[1a]

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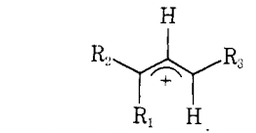
The 2-phenyl-2-penten-4-yl cation (**4**) has been prepared in magic acid solution at −120 °C from 2-phenyl-3-penten-2-ol. Upon raising the temperature, a cyclic ion **12** was observed at −80 °C, which finally rearranged to the indanyl cation **14** at −70 °C. Methyl and deuterium substitution of the phenyl ring allowed identification of the structure of the intermediate ions and determination of the mechanism of the cyclization process.

A large number of stable alkyl-substituted allyl cations have been prepared and investigated[2] in superacidic media, but very few phenylallyl cations[3] are known as stable species at low temperature. At first glance this seems to be surprising since phenyl groups in most other carbocations have been shown to exhibit a greater stabilizing ability than alkyl groups.[4] However, in contrast to alkylated allyl cations, phenylallyl cations can easily undergo intramolecular cyclization to the corresponding indanyl cations, which explains the difficulty in obtaining them as stable species.[3a,b]

While ions **1**, **2**, and **3** were reported to be observable from −50 to −70 °C in FSO_3H–SO_2 or SO_2ClF, **4** could not be detected under these conditions since it rearranged to **14** (Scheme I). A deprotonation–reprotonation sequence was suggested to cause this rearrangement.[3b] Since deprotonation should be less favored in more acidic media, phenylallyl cations are expected to be more stable in FSO_3H–SbF_5–SO_2ClF than in FSO_3H–SO_2. Therefore, we attempted to prepare **4** in magic acid solution and to study its rearrangement under these conditions.

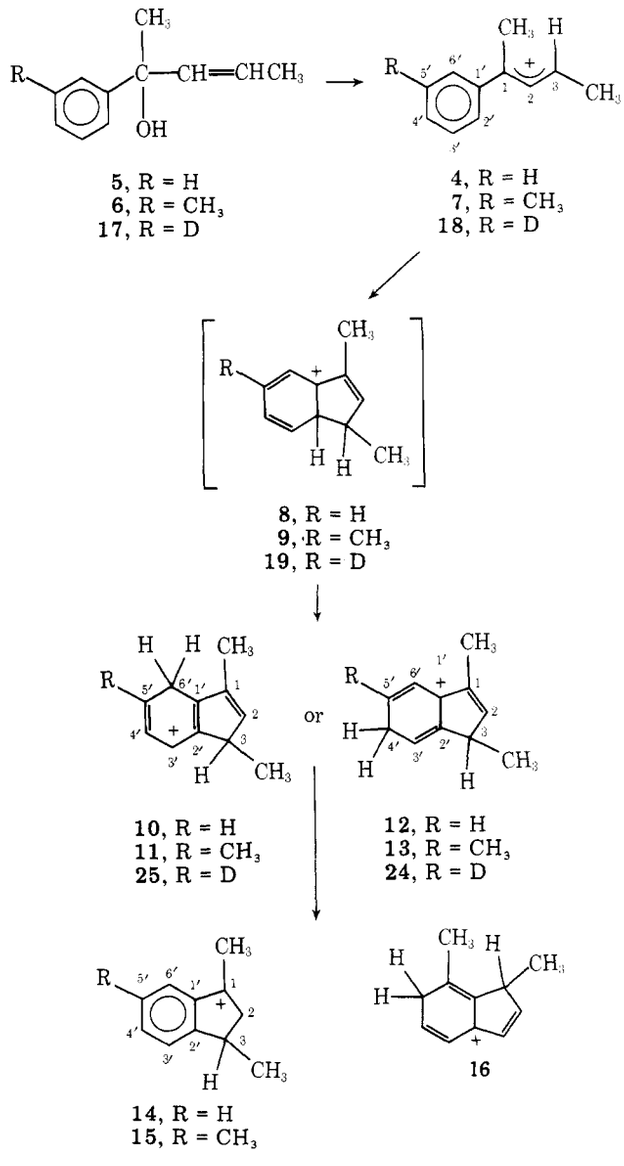


1, $R_1 = CH_3$; $R_2 = R_3 = Ph$
2, $R_1 = R_2 = R_3 = Ph$
3, $R_1 = H$; $R_2 = Ph$; $R_3 = CH_3$
4, $R_1 = R_3 = CH_3$; $R_2 = Ph$

Results and Discussion

When a precooled solution of 2-phenyl-3-penten-2-ol (**5**) in SO_2ClF was slowly added with good stirring to an excess of FSO_3H–SbF_5 in SO_2ClF at −120 °C, the 2-phenylpentenyl cation **4** was obtained. It is stable below −90 °C but starts to rearrange at this temperature (Scheme I). Ion **4** was characterized by its ^1H NMR and ^{13}C NMR spectra (Tables I and II). Conversion of **4** into another ion was observed at −80 °C. This species, however, could not be obtained with complete purity since contamination resulting from rearrangement to the known indanyl cation **14** began to occur at −70 °C. Both

Scheme I



5, R = H
6, R = CH_3
17, R = D

4, R = H
7, R = CH_3
18, R = D

8, R = H
9, R = CH_3
19, R = D

10, R = H
11, R = CH_3
25, R = D

12, R = H
13, R = CH_3
24, R = D

14, R = H
15, R = CH_3

16

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Table I. ^{1}H NMR Chemical Shifts (δ) and Multiplicities of Phenylallyl Cations and Their Rearrangement Products

Registry no.	Compd	H(2)	H(3)	H(3′)	H(4′)	H(5′)	H(6′)	Methyl substituents
64999-96-8	4	Aromatic and olefinic protons absorb in a multiplet at 8.3–9.3						C(1)–CH_3 3.6, C(3)–CH_3 3.0 (d)
65027-47-6	12	8.6	4.3	8.6	4.7	8.9	8.2 (d)	C(1)–CH_3 2.7, C(3)–CH_3 1.9 (d)
65036-43-3	13	8.3	4.2	8.3	4.6	–	8.0 (s)	C(1)–CH_3 2.6, C(3)–CH_3 1.7 (d), C(5′)–CH_3 3.0
64999-59-3	14	4.1	3.7	8.1	8.6	8.0	8.6	C(1)–CH_3 3.5, C(3)–CH_3 1.7 (d)
64999-58-2	15	4.2	3.8	8.0	8.4	–	8.3 (s)	C(1)–CH_3 3.7, C(3)–CH_3 1.8 (d), C(5′)–CH_3 2.6

Table II. ^{13}C NMR Chemical Shifts (ppm Downfield of Me_4Si) and Multiplicities of Phenylallyl Cations and Their Rearrangement Products

	C(1)	C(2)	C(3)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	Methyl substituents
4	213.7 (s)	136.3 (d)	190.8 (d)	137.8 (s)	135.6 (d)[a]	131.0 (d)	147.3 (d)	131.0 (d)	131.6 (d)[a]	C(1)–CH_3 25.7,[a] C(3)–CH_3 21.6[a]
12	152.9 (s)[a]	181.1 (d)[a]	46.0 (d)	187.4 (s)	146.4 (s)[a]	158.1 (d)[a]	42.5 (t)	171.5 (d)[a]	126.4 (d)	C(1)–CH_3 12.4,[a] C(3)–CH_3 11.1[a]
13	150.7 (s)[a]	175.5 (d)[a]	45.1 (d)	186.4 (s)	145.1 (s)[a]	154.3 (d)[a]	45.6 (t)	191.8 (s)	125.2 (d)	C(1)–CH_3 13.1,[a] C(3)–CH_3 11.2,[a] C(5′)–CH_3 25.4
14	251.8 (s)	56.5 (t)	41.9 (d)	143.9 (s)	184.4 (s)	132.0 (d)[a]	153.9 (d)	128.1 (d)[a]	134.7 (d)[a]	C(1)–CH_3 24.4, C(3)–CH_3 16.9

[a] Relative assignment is uncertain.

isomerizations were irreversible, as demonstrated by recooling the samples to −120 °C. The benzenium ion **8**, which might result from the electrocyclic ring closure of **4**, was eliminated as the intermediate observed at −80 °C on the basis of the ^{13}C NMR spectrum. This spectrum shows three vinylic singlets and four vinylic doublets, while the spectrum of **8** is expected to display two singlets and five doublets in the same region. Therefore, **10** and/or **12** are suggested as possible observable intermediates in the rearrangement sequence **4** → **14**.

In order to differentiate between these two arenium ions, 2-(*m*-tolyl)-3-penten-2-ol (**6**) was treated with FSO_3H–SbF_5. Even at −120 °C **7** could only be observed as a minor component in the spectrum of the cyclic intermediate. Rearrangement to the indanyl cation **15** occurred at −60 °C. As expected for both **11** and **13**, the ^{13}C NMR spectrum of the intermediate ion showed four olefinic singlets and three olefinic doublets.

Based on the ^{1}H NMR spectrum, the identification of **13** was possible. Since H(6′) of **13** is the only proton attached to an even numbered carbon in the heptatrienyl backbone, it should be the most shielded olefinic proton. For the same reason, H(4′) should be the most shielded vinylic hydrogen in **11**. Figure 1b clearly shows that the olefinic resonance at highest field is a singlet, in accord with H(6′) of **13**. On the contrary, H(4′) of **11** should display a doublet.

Analogously, the high-field absorption of Figure 1a can be assigned to H(6′) of **12**, a doublet split by H(5′), whereas H(4′) of **10** should show a triplet. As observed previously with other benzenium ions,[5] the methylene group of both **12** and **13** absorbed as a broad singlet. Only trace amounts of **16** could be detected together with **12**, indicating that in the allyl cation **7** C(3) attacks selectively at the C(2′) position to yield the corresponding arenium ion **9**.

Mechanism. As depicted in Scheme I, the electrocyclic ring closure of **4** and **7** to **8** and **9** is proposed to be the initial step. Further rearrangements by a series of two 1,2-hydride shifts yield **12** and **13**, respectively. A deprotonation–reprotonation sequence cannot be accountable for the formation of **12** and **13** since this would imply protonation of indenes on the aromatic ring. This hypothesis, however, is in contrast to the observation that indanyl cations do not show deuterium incorporation in their six-membered rings when they are prepared from phenylallyl alcohols and FSO_3D.[3] The observation that **7** cyclizes faster than **4** can be explained by the fact that

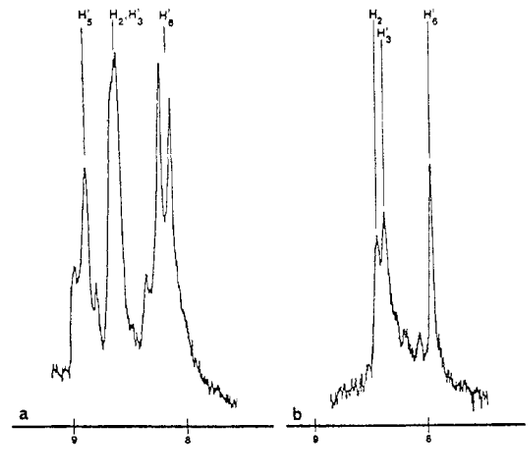


Figure 1. ^{1}H NMR spectra (olefinic protons) of (a) ion **12** and (b) ion **13** at 100 MHz.

the additional methyl group (R) stabilizes the allyl cation **7**, where R is attached to an uncharged carbon atom. The formation of **12** and **13** furthermore demonstrates that the 1,2-hydride shifts are kinetically preferred over a 1,8-hydride shift, which would yield **14** and **15** directly from **8** and **9**.

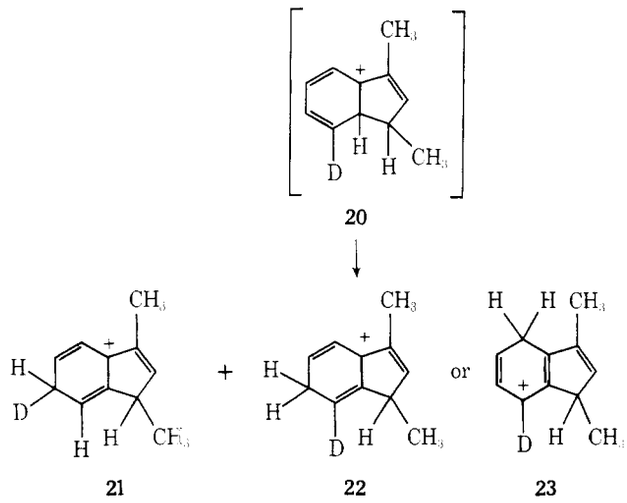
12 may be regarded as a benzenium ion with a vinyl substituent in the para position, whereas **10** is a benzenium ion with an *o*-vinyl group. It is well-known that alkylbenzenes yield *p*-alkylbenzenium ions when dissolved in strong acids.[5] Therefore, we suggest that **12** can be observed as an intermediate because it is the thermodynamically most stable arenium ion.

Finally, the formation of **14** can proceed either via a series of intramolecular hydride shifts or via a deprotonation–reprotonation mechanism.

In order to prove the suggested reaction mechanism, we prepared the meta-deuterated alcohol **17** and studied its ionization and further cyclization (Scheme II). Since secondary kinetic isotope effects are generally small, we expected **18** to yield equal amounts of **19** and **20**. At −80 °C these products then rearranged to the benzenium ions **24** and **21** + **22**, respectively. As expected for a mixture of these ions, the most shielded olefinic absorptions were a doublet (H(6′) of **21** and **22**) and a singlet (H(6′) of **24**) centered at δ 8.2. Since both

Scheme II

17 → 18 → 19 → 24 or 25



of the alternative structures, **23** and **25**, should show doublets at δ 8.2, the identity of the intermediates could be confirmed by this experiment.

However, the singlet (**24**) was of lower intensity than the doublet (**21** + **22**), indicating a loss of deuterium from the 5′ position. Since a deprotonation–reprotonation mechanism was already excluded above, we suggest that in the cyclic intermediates (e.g., **24**) slow 1,2-hydride migrations are taking place, yielding small equilibrium concentrations of isomeric benzenium ions. In this equilibration process deuterium can be washed out of the 5′ position to yield the observed spectrum.

The formation of **14** has already been observed by Pittman and Miller[3b] when **5** was treated with FSO_3H at −70 °C. Neither **4** nor **12** have been observed under these conditions. Therefore, we treated **5** with FSO_3H–SO_2ClF at −120 °C. In contrast to our observations in magic acid, the indanyl cation **14** was not formed, even at −120 °C. Therefore, it is proposed that when magic acid is substituted for an acid of lower acidity another mechanism becomes operative. In such media an alternative route is deprotonation to a transient indene and a subsequent reprotonation, as proposed by Pittman and Miller.[3b]

Experimental Section

Materials. Magic acid was prepared from triply distilled FSO_3H and doubly distilled SbF_5; a 1:1 molar ratio was used in all experiments. 2-Phenyl-3-penten-2-ol (**5**) was commercially available (Chemical Samples Co.).

2-(*m*-Tolyl)-3-penten-2-ol (6) was prepared from *m*-methylacetophenone (Aldrich Chemical Co.) and 1-propenylmagnesium bromide (obtained from 1-bromo-1-propene, Chemical Samples Co.) in THF: bp 104 °C (4 mm); ^1H NMR (CCl_4) δ 1.5 (d, 3 H, J = 4 Hz, CH_3), 1.6 (s, 3 H, CH_3), 5.5 (m, 2 H, olefinic CH), 7.1 (m, 4 H, phenyl CH).

2-(*m*-Deuteriophenyl)-3-penten-2-ol (17). *m*-Bromoacetophenone (Eastman) was converted into its ethylene ketal by refluxing and stirring with ethylene glycol and a small amount of *p*-toluenesulfonic acid in petroleum ether (bp 35–55 °C) for 36 h: ^1H NMR (CCl_4) δ 1.9 (s, 3 H, CH_3), 4.1 (m, 4 H, CH_2), 7.7 (m, CH).

The ethylene ketal was treated with magnesium turnings in THF, and the Grignard compound was then hydrolyzed with D_2O–D_2SO_4 at room temperature to give *m*-deuterioacetophenone. Deuterium incorporation was ascertained by the observed 4:3 phenyl CH/CH_3 proton ratio, the substantial simplification of the ring proton absorption in the ^1H NMR spectrum, and the ^2H NMR spectrum (absorption at δ 7.6).

17 was prepared by reacting *m*-deuterioacetophenone with 1-propenylmagnesium bromide in THF: bp 54–55 °C (0.1 mm); ^2H NMR (acetone) δ 7.6 (relative to internal acetone-d_6).

Preparation of Ions. A dilute solution of the corresponding alcohol in SO_2ClF at −120 °C was added dropwise with good stirring to an approximately 1:2 (by volume) solution of FSO_3H–SbF_5 in SO_2ClF at −120 °C. The preparation of **4** and **18** required extremely slow addition to avoid further rearrangement due to local heating. Intermediate ions **12**, **21**, **22**, and **24** (observed at −90 °C) were prepared by warming up the former solutions by a careful increase of the probe temperature in the ^1H NMR or ^{13}C NMR spectrometers, and they were stable up to −80 °C. Ion **13** was observed in the original solution even at −120 °C and was stable up to −70 °C. The spectra of indanyl cations **14** and **15** were recorded at −60 °C.

Proton Magnetic Resonance Spectra. ^1H NMR spectra were obtained on a Varian Associates Model A56/60A or HA-100 spectrometer equipped with a variable-temperature probe. External Me_4Si (capillary) was used as a reference for the carbenium ions and internal Me_4Si for their precursors.

Carbon-13 Magnetic Resonance Spectra. The spectrometer used was a Varian Associates Model XL-100 equipped with a broad band decoupler and variable-temperature probe. Chemical shifts were measured from external (capillary) Me_4Si.

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Registry No.—**5**, 4743-67-3; **6**, 64999-97-9; **17**, 64999-98-0; *m*-deuterioacetophenone, 64999-99-1; *m*-methylacetophenone, 585-74-0; 1-bromo-1-propene, 590-14-7.

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