for 4 hr. The solution was concentrated and chromatographed over alumina with benzene. Evaporation of the solvent left an almost colorless material, which was recrystallized from methylcyclohexane. The yield of **6**, mp 210–211.5°, was 231 mg (69%). *Anal.* Calcd for $C_{18}H_8S_4$: C, 61.33; H, 2.29; S, 36.38. Found: C, 61.4; H, 2.5; S, 36.0.

The helicenes **7**, **8**, **9**, and **10** were prepared according to a procedure identical with that of the preparation of **6**.

Naphtho[1,2-*d*]thieno[3,2-*d*′]benzo[1,2-*b*:4,3-*b*′]dithiophene (7). The helicene **7** was prepared by irradiation for 1.5 hr of a suspension of **16** (420 mg, 1.2 mmol) in 550 ml of benzene to which 10 mg of iodine was added. The yield of **7**, mp 220–222°, was 249 mg (60%). *Anal.* Calcd for $C_{20}H_{10}S_3$: C, 69.23; H, 2.91; S, 27.76. Found: C, 69.3; H, 3.0; S, 27.8.

Dithieno[3,2-*e*:3′,2′-*e*′][1]benzothieno[2,3-*b*][1]benzothiophene (8). The helicene **8** was prepared by irradiation for 1 hr of a suspension of **19** (50 mg, 0.14 mmol) in 550 ml of benzene to which 5 mg of iodine was added. The yield of **8**, mp 279–280°, was 25 mg (51%). *Anal.* Calcd for $C_{18}H_8S_4$: C, 61.33; H, 2.29; S, 36.38. Found: C, 61.4; H, 2.3; S, 36.1.

Dibenzo[*e*:*e*′][1]benzothieno[2,3-*b*][1]benzothiophene (9). The helicene **9** was prepared by irradiation for 1.5 hr of a suspension of **20** (100 mg, 0.29 mmol) in 550 ml of benzene to which 5 mg of iodine was added. The yield of **9**, mp 289–291.5°, was 50 mg (50%). *Anal.* Calcd for $C_{22}H_{12}S_2$: C, 77.60; H, 3.56; S, 18.83. Found: C, 77.6; H, 3.7; S, 18.8.

Naphtho[2′,1′-*b*′]thieno[4,′5′-*f*]naphtho[2,1-*b*]thiophene (10). The helicene **10** was prepared by irradiation for 2 hr of a suspension of **25** (300 mg, 0.87 mmol) in 550 ml of benzene to which 20 mg of iodine was added. The yield of **10**, mp 240–241°, was 146 mg (50%). *Anal.* Calcd for $C_{22}H_{12}S_2$: C, 77.60, H, 3.56; S, 18.83. Found: C, 77.7; H, 3.7; S, 18.8.

Acknowledgment. We thank Drs. J. Runsink and Dr. J. Lugtenburg for their help in the interpretation of the nmr spectra.

Stable Carbocations. CXLII.[1] 1-Acenaphthenium Ions

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Abstract: The 1-acenaphthenium ion **1a** and several of its substituted derivatives were directly observed in superacid solutions and were characterized by proton and carbon-13 nuclear magnetic resonance spectroscopy. Spectroscopic data show that positive charge is heavily delocalized into one of the naphthalene rings indicating the classical nature of these ions. The intramolecular degenerate 1,2-hydrogen shift in 1,2-dimethyl- and 1-methyl-2-ethyl-1-acenaphthenium ions was studied by pmr spectroscopy. The parent 1-acenaphthenium ion and 1,2,2-trimethyl-1-acenaphthenium ions undergo no 1,2-hydrogen shift or methyl shift in the temperature range studied.

In a study of acid-catalyzed polymerization, Gandini and Plesch[3] claimed on the basis of ultraviolet spectral data that they observed the secondary carbenium ion **1a** when acenaphthylene was treated with concentrated sulfuric acid. Young,[4] however, in an extension to their work concluded that the species observed by Gandini and Plesch was not the 1-acenaphthenium ion but more likely a dimeric cation.

We wish to report the first unambiguous preparation of the 1-acenaphthenium ion and show from proton and carbon-13 nmr spectral data that it is a secondary nonequilibrating carbenium ion in the temperature range −90 to 40°. This contrasts with the results for a number of other arylcarbenium ions[5] which undergo fast intramolecular 1,2-hydrogen and 1,2-methyl shifts in a similar temperature range. Fast intramolecular 1,2-hydrogen shifts have been found to occur in substituted arenium ions,[6] and recently in the parent benzenium ion.[7] The rates of such processes appear to vary over a wide range. 1,2-Methyl shifts in benzenium ions have been found to be very slow processes in comparison to the 1,2-hydrogen shifts.[6a,b,8] In superacid media and some other acid systems,[6b,8] equilibrations in acyclic and alicyclic carbenium ions[9,10] which occur *via* 1,2-hydrogen or methyl shifts have also been examined by nuclear magnetic resonance. In most cases, the intramolecular hydrogen or methyl shift is fast and strongly dependent on the structure of the carbenium (or arenium) ion. Rates and activation parameters for the 9,10-methyl shift in 9,10,10-trimethylphenanthrenium ion have recently been determined by means of nmr spectroscopy.[11] In this system, the rate of the 1,2-methyl shift is nearly as fast as the 1,2-hydrogen shift in methylbenzenium ions. Furthermore, the relative migratory tendencies of aryl groups in the

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(2) Postdoctoral Research Associate, 1971–1973.

(3) A. Gandini and P. H. Plesch, *J. Chem. Soc. B*, 7 (1966); 4765 (1965).

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(8) G. A. Olah and J. A. Olah, ref 6a, Chapter 17.

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(11) (a) V. G. Shubin, D. V. Korchagina, A. I. Rezunkhinard, and V. A. Koptyug, *Dokl. Akad. Nauk SSSR*, **179**, 119 (1968); (b) V. G. Shubin, D. V. Korchagina, B. G. Derendyaev, V. I. Mamatyuk, and V. A. Koptyug, *Zh. Org. Khim.*, **6**, 2066 (1970); (c) D. V. Korchagina, A. Koptyug, B. G. Derendyaev, and V. G. Shubin, *ibid.*, **7**, 2582 (1971); (d) H. Volz, G. Zimmermann, and B. Schelberger, *Tetrahedron Lett.*, 2429 (1970).

Table I. ^1H Nmr Parameters of 1-Acenaphthenium Cations[a]

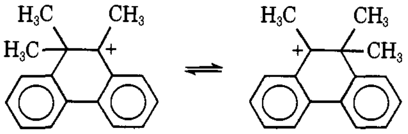
Cation	CH_3	$*CH_2CH_3$	H_1	H_2	H_3,H_4, H_5,H_7	H_6	H_8	Other
1a			10.65[b]	5.20	8.4–8.9	9.85	9.5	
1b	3.75			5.10	8.3–8.8	9.58	9.42	
1c	2.0 (t)[c]	4.21 (q)[c]		5.20	8.3–8.8	9.60	9.45	
1d				4.80 (s)	8.0–8.5	9.08	8.92	12.7 (OH)
2a	2.0 (d) 3.6 (s)			4.90	8.2–8.7	9.55	9.35	
2b	0.85 (t) 3.60 (s)	2.75		4.95	8.1–8.6	9.45	9.22	
3a	1.90 (s) 3.45 (s)				8.1–8.5	9.38	9.15	
3b	1.90 (s) 1.90 (t)	3.82 (q)			8.1–8.5	9.35	9.20	
3c	0.60 1.90 3.50	2.60			8.2–8.6	9.45	9.20	

[a] 60 MHz, in δ (ppm), relative to external tetramethylsilane as reference. [b] d = doublet, q = quartet, s = singlet, t = triplet, m = multiplet. [c] $J = 7.0$ Hz.

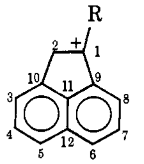
Table II. Carbon-13 Nmr Parameters of 1-Acenaphthenium Cations and Their Reference Cations[a]

Cation	C_1	C_2	C_3,C_4, C_5,C_7	C_6	C_8	$C_9,C_{10}, C_{11},C_{12}$	C_3	$*CH_2CH_3$
1a	−6.4	148.7	64.8, 66.1 71.0, 72.8	37.7	61.8	46.1, 54.0 62.8, 69.3		
1b	−36.7	140.7	53.6, 60.3 62.0, 63.9	35.2	51.2	44.9, 47.8 54.0, 62.0	168.4	
1c	−41.1	142.7	59.3, 60.9 62.8, 67.7	35.5	51.9	45.5, 51.0 54.1, 61.4	178.1	160.8
1d	−23.5	150.1	61.8, 63.0 65.2, 66.1	47.2	61.8	47.7, 53.6 60.4, 62.4		
2a	−29.7	134.9	59.3, 60.9 62.2, 63.0	34.4	51.8	46.0, 49.2 57.8, 61.9	170.6 178.5	
3a	−40.7	131.1	53.1, 60.8 63.3, 63.7	34.6	50.8	44.4, 47.7 53.1, 61.5	169.7 172.2 (2C)	
4[b]	−7.6		57.7, 58.3 62.6, 69.6	25.6	54.7	41.5, 53.1 55.0, 61.6	162.7	
7[b]	−39.5		58.4, 58.7 64.0, 65.3	35.5	55.9	42.3, 50.8 57.8, 58.7	155.9 159.5	
9	−9.7	161.2	62.4, 64.6 71.4, 71.6	49.8	61.2	57.6, 57.9 61.7, 68.7		
10	−21.7		60.9, 63.2 66.1, 67.7	42.2	58.1	44.6, 57.8 60.5, 65.9	165.2	
11	−6.4						163.5	

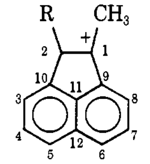
[a] See Experimental Section. [b] Numbering system used for naphthalene ring is identical with that in the acenaphthene molecule.



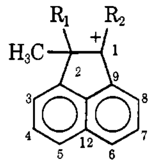
doubly degenerate rearrangement of stable 9-aryl-9,10-dimethylphenanthrenium ions have recently been established.[12] These studies induced us to report our investigations on several 1- and 1,2-substituted acenaphthenium ions (**1**, **2**, and **3**), and the important differences observed between phenanthrenium and acenaphthenium ions. The present work was concerned with the preparation and observation of a series of acenaphthenium ions under stable ion conditions and investigation of the mechanism of 1,2-shift reactions which occur between the C_1 and C_2 carbon atoms of these ions.



1a, R = H
b, R = CH_3
c, R = CH_2CH_3
d, R = OH



2a, R = CH_3
b, R = CH_2CH_3



3a, $R_1 = CH_3$; $R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = CH_2CH_3$
c, $R_1 = CH_2CH_3$; $R_2 = CH_3$

Results and Discussion

A description of the preparation of the following ions is provided in the Experimental Section. Proton and carbon-13 chemical shifts are summarized in Tables I and II, respectively. Assignments were made on the basis of comparisons with the spectra of model compounds, and in the case of the cmr spectra, from "off-resonance" decoupling experiments.[13]

A. 1-Acenaphthenium ion (1a) is generated by the careful addition of a cold suspension of 1-acenaphthenol (**2**) in SO_2ClF at −78°, to either SbF_5 or FSO_3H-SbF_5 (1 :1) in SO_2ClF solution at the same temperature. The 60-MHz pmr spectrum of ion **1a** (Figure 1a) consists of a singlet at δ 5.2 ppm (2 protons) for the C_2 methylene protons, an aromatic multiplet centered at

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(12) V. G. Shubin, D. V. Korchagina, G. I. Borodkin, B. G. Derendjaev, and V. A. Koptyug, *Chem. Commun.*, 696 (1970).

(13) H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 7445 (1969).

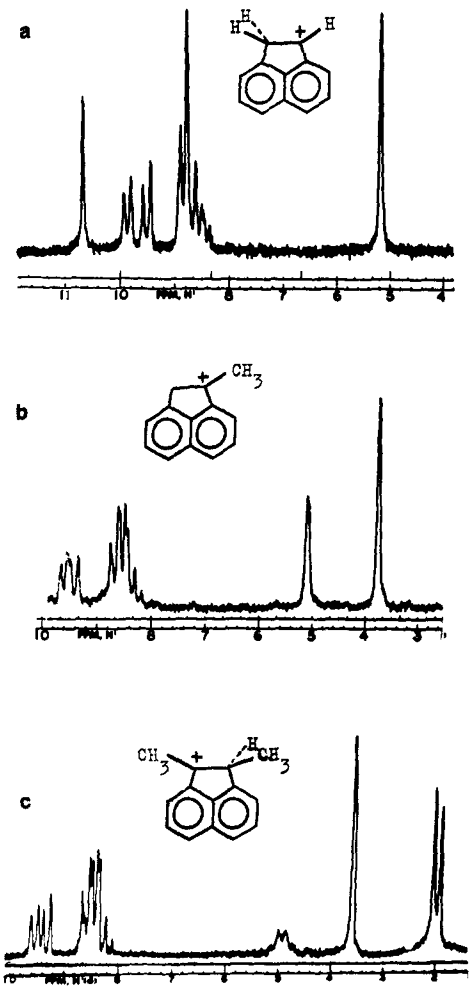
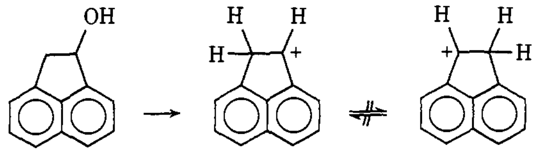


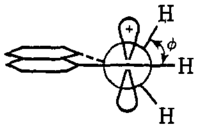
Figure 1. (a) The 60-MHz pmr spectrum of 1-acenaphthenium ion at −78°; (b) 60-MHz pmr spectrum of 1-methyl-1-acenaphthenium ion at −78°; (c) 60-MHz pmr spectrum of 1,2-dimethyl-1-acenaphthenium ion at −70°.



2 **1a**

δ 8.4–9.0 ppm (4 protons) for the C_3, C_4, C_5, and C_7 protons, two sets of doublets centered at δ 9.5 (one proton, J = 8.0 Hz), and δ 9.85 (one proton, J = 7.2 Hz) for the C_6 and C_8 protons, respectively; and a singlet at δ 10.65 (one proton) for the C_1 proton. Ion **1a** is stable at temperatures from −90 to +40° (pressure nmr tube). It quickly decomposed at temperatures above +40°. The spectrum of the ion in the above temperature range was independent of temperature. The absence of a 1,2-hydrogen shift is surprising, for similar shifts are generally observed in related systems.[11,12] We consider it due to the unique geometry of the fixed five-membered ring in ion **1a**. Considerable strain must exist within the molecule, thus the C_1–C_2 bond length should be somewhat longer than that of a normal sp^3–sp^2 bond. The rigid structure of the acenaphthene molecule would suffer additional strain in the transition state of an intramolecular 1,2-hydrogen shift process. Models show that the five-membered ring cannot be easily twisted (or deformed) in order to reach suitable geometry for the hydrogen to migrate from C_1 to C_2.

No coupling between the C_1 proton and the C_2 methylene protons is observed in the pmr spectrum of ion **1a**. Examination of models show that the dihedral angle (ϕ) is such that on the basis of the Karplus expression,[14]



an almost negligible vicinal proton–proton coupling constant is expected.

The observation of a nonequilibrating 1-acenaphthenium ion is the first example of a system with a methylene group adjacent to a positively charged carbon atom where a rapid 1,2-hydrogen exchange process does not occur. A typical example of a cation where such a 1,2-hydrogen shift occurs is the degenerate cyclopentyl cation reported by this laboratory.[10] The reason hydrogen shifts occur readily in this cation but not in ion **1a** may be due to factors apart from the unfavorable stereochemistry in the latter ion. The energy difference between the classical ionic structure and the transition state for a hydrogen shift is most likely greater for the acenaphthene system than for the cyclopentane system. This is a result of resonance and ring strain effects which lower the energy of the classical ion to a greater extent than the bridged structure. These effects operate to a much lesser extent in the cyclopentyl cation.

A high barrier for the 1,2-hydrogen shift in ion **1a** is consistent with the mechanistic study, by Dewar and Fahey,[15] of the polar addition reactions of acenaphthylene. The structure of the transition state for the hydrogen shift resembles that of a "π complex." However, the stereochemical course of the addition reaction of deuterium chloride and bromide to acenaphthylene suggest that a π complex is not involved as an intermediate in these reactions, but rather the carbenium ion **1a**.

The carbon-13 nmr spectrum of ion **1a** indicated a chemical shift for the carbenium carbon (C_1) of −6.4 ppm from CS_2, which is very close to the corresponding shift in the reference cation methylnaphthylcarbenium ion **4** (Table II). If it is assumed there is a direct relationship between the π-electron density at an sp^2 hybridized cation atom and the carbon chemical shift, then the carbenium carbon chemical shifts in ions **1a** and **4**, as well as the para-carbon shifts (C_6 in **1a**), indicate a substantial amount of charge delocalization into the naphthalene ring. Ring-strain effects may also contribute to the C-1 chemical shift in **1a**.

B. 1-Methyl-1-acenaphthenium ion (1b) is generated in either FSO_3H–SO_2ClF or FSO_3H–SbF_5–SO_2ClF solutions at −78° from the parent alcohol **5** or through the rearrangement of the unstable 2-methyl-1-acenaphthenium ion **1b′** which can be generated from a mixture of *cis*- and *trans*-2-methyl-1-acenaphthenol (**6**). We have found that the rearrangement of ion **1b′** into ion **1b** takes place very rapidly even at low temperature. The pmr spectrum (Figure 1b) of the solution obtained

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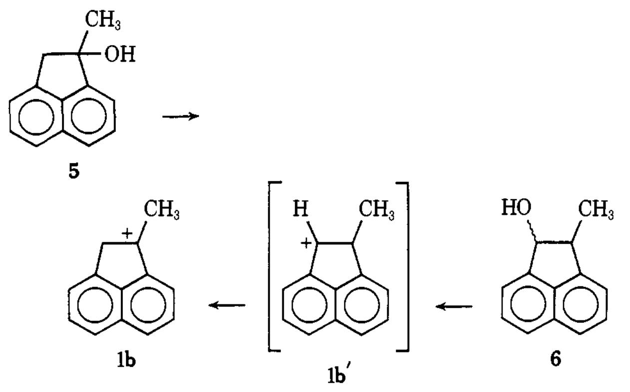
(15) (a) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2248 (1963).

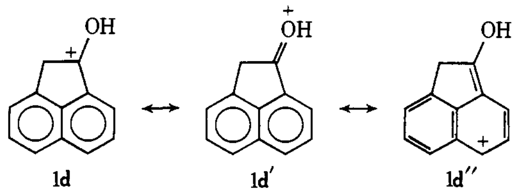


by the ionization of **6** at −120° corresponds exactly with the pmr spectrum of ion **1b**. The stability of ion **1b** is due to the greater stability of a tertiary ion over that of a secondary ion, so that even the unfavorable 1,2-hydrogen shift takes place at low temperature.

The 60-MHz pmr spectrum of ion **1b** consists of a singlet at δ 3.75 (three protons) for the C_1 methyl protons, a singlet at δ 5.1 (two protons) for the C_2 methylene protons, a multiplet extending from δ 8.3–8.8 (four protons) for the C_3, C_4, C_5, and C_7 protons, and two sets of doublets centered at δ 9.42 (one proton, J = 8.0 Hz) and 9.58 (one proton, J = 8.0 Hz) for the C_6 and C_8 protons, respectively. Ion **1b** is stable from −90 to +80°, but gradually decomposes at higher temperatures. The appearance of the pmr spectrum in the above temperature range is independent of temperature. The process **1b** $\rightleftharpoons$ **1b′** is not observed, indicating that a high-energy barrier must be overcome for the secondary hydrogen to migrate by an intramolecular process to the tertiary carbenium center. In the parent 1-acenaphthenium ion (**1a**), the barrier for a secondary 1,2-hydrogen shift is high, not only because of the rigid geometry of the incorporated five-membered ring, but also because most of the positive charge at the carbenium carbon has been delocalized into the naphthalene ring. The latter effect is reflected by a more shielded C_1 carbenium carbon shift ($\delta_{^{13}C}$ −6.4; see Table II) in ion **1a** than in the other acenaphthene derivatives (even if allowance is made for the alkyl substituent effect). In ion **1b** more positive charge is localized at the carbenium carbon ($\delta_{^{13}C}$ −36.7). Thus a 1,2-hydrogen shift to form ion **1b′** might be expected to occur more readily than in ion **1a**. However, it is not observed, so the energy barrier must still be too high for such a process. Ion **1b** does not show more delocalization of positive charge into the naphthalene ring than its reference cation, dimethylnaphthylcarbenium ion (**7**), as is shown by the carbon nmr chemical shifts of their carbenium carbon centers ($\delta_{^{13}C}$ −36.7 and −39.5, respectively). The difference in the carbenium carbon chemical shifts between ions **1b** and **7** ($\Delta\delta_{^{13}C}$ +2.8) is approximately the same size as that between ions **1a** and **4** ($\Delta\delta_{^{13}C}$ +1.2). Two different methyl group carbon signals are observed in ion **7** ($\delta_{^{13}C}$ +155.9 and +159.9) so that, apparently, free rotation of the dimethylcarbinyl group about the C_1–C_α bond is restricted.

C. **1-Ethyl-1-acenaphthenium ion (1c)** was generated from 1-ethyl-1-acenaphthenol (**8**) using the same procedure as that for the preparation of ion **1b**. The pmr spectrum of ion **1c** is similar to that of ion **1b**, and its pmr parameters are summarized in Table I. Warming the cation solution at +80° does not cause any change in the pmr signals. Ion **1c** gradually decomposed at higher temperatures. An intramolecular 1,2-hydrogen shift process is unfavorable for the same reason as that mentioned above for ion **1b**. The carbon shift of the carbenium carbon in **1c** ($\delta_{^{13}C}$ −41.1) is about 5 ppm more deshielded than that in **1b**.

D. **1-Hydroxy-1-acenaphthenium ion (1d)** was generated from 1-acenaphthenone (**9**) by protonation with FSO_3H or FSO_3H–SbF_5 (1:1) diluted with SO_2ClF (SO_2) at −78°. Pmr parameters are summarized in Table I. The chemical shift of the proton bonded to the oxygen atom is found as a broad singlet at δ 12.7 which is shielded about 2 ppm from the OH resonance in protonated aliphatic ketones,[16a] and about 1 ppm from the same peak in protonated alkyl aryl ketones.[16b] In a study of several protonated para-substituted acetophenones, a correlation was found between the OH proton chemical shift and the σ^+ values for the substituents. The above data and others for di- and trihydroxycarbenium ions[17] indicate that the OH proton chemical shift is a good indicator of the electron-withdrawing ability of the groups attached to the protonated keto group. Therefore, the shielded OH signal for ion **1d** suggests that there is substantial charge delocalization into the naphthalene ring and that resonance forms **1d** and **1d′** are of lesser importance in this ion than in protonated aliphatic ketones. The carbon-13 nmr data also support this conclusion. The C-1 resonance in ion **1d** is found to have a value $\delta_{^{13}C}$ −23.5, which is about 14 ppm more deshielded than the corresponding carbon resonance in the precursor **9**. In protonated ketones where resonance forms similar to **1d″** are of minor importance a much larger deshielding is usually observed (for example, 32.2 ppm in acetone). The dependence of the chemical shift of an sp^2 hybridized carbon atom bonded to oxygen, and the π-electron density at that carbon, has been established by Olah and White[17] in a set of semiempirical calculations.



The deshielding of the C-1 resonance in ketone **9**, which occurs on protonation, is similar to that observed for the model compound, 1-acetonaphthone (**10**). Protonation of the carbonyl group in this compound results in a shift of the carbonyl carbon resonance from $\delta_{^{13}C}$ −6.4 to $\delta_{^{13}C}$ −21.7 ($\Delta\delta_{^{13}C}$ 15.3).

E. **1,2-Dimethyl-1-acenaphthenium ion (2a)** was generated in either FSO_3H–SO_2ClF or FSO_3H–SbF_5–SO_2ClF solutions at −78° from the parent alcohol, or from a mixture of *cis*- and *trans*-1,2-dimethyl-1-acenaphthenol (**12**), or through the rearrangement of the unstable 2,2-dimethyl-1-acenaphthenium cation (**13**), which in turn is formed directly from 2,2-dimethyl-1-acenaphthenol (**14**).

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(17) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **90**, 1884 (1968).

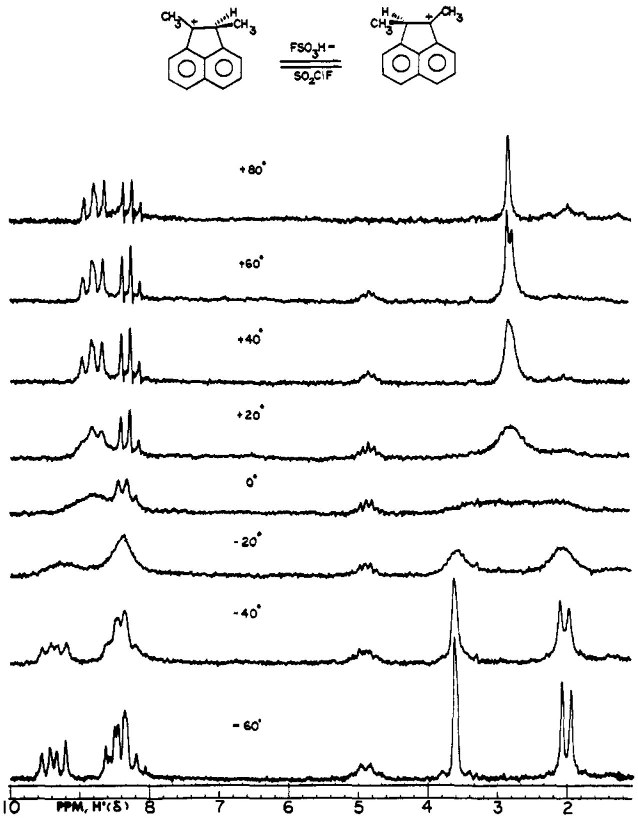
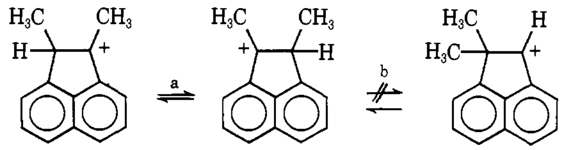


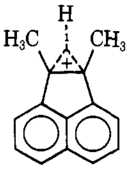
Figure 2. The 60-MHz pmr spectra of 1,2-dimethyl-1-acenaphthenium ion **2a** in the temperature range −60 to +80°.



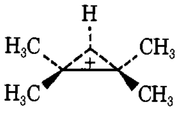
2a **13**

The 1,2-dimethyl-1-acenaphthenium ion (**2a**) was found to be a nonequilibrating ion below −60° (Figure 1c). An increase in the temperature leads to a broadening of all peaks (Figure 2), which on further warming again become sharp. The observed spectral changes in the temperature range, −60 to +80°, are completely reversible, and consistent with a pair of carbenium ions rapidly equilibrating *via* an intramolecular 1,2-hydrogen shift (pathway a), but not *via* a 1,2-methyl shift process (pathway b). It can be concluded from the observation at +60° of the multiple coupling in the C_2 methine signal, and the methyl doublet signal, that 2,2-dimethyl-1-acenaphthenium ion (**13**) is not being formed *via* a reversible 1,2-methyl shift (pathway b). If a 1,2-methyl shift does take place, the observed average shift for the methine proton signal should be at much lower field ($\delta\ ^1/_2(5.0 + 10.7) = 7.85$ ppm) than the observed value (4.9 ppm). In addition, the coupling constant between the rapidly shifted proton with the six equivalent protons on the two methyl groups should be equal to half of the value in the static ion **2a** ($J = {}^1/_2$ (8 Hz) = 4 Hz). The observed splitting of the heptet (4 Hz) confirms the rapid 1,2-hydrogen shift mechanism. The drastic change of all the aromatic signals also suggests the same conclusion. In the rapidly equilibrating pair of ions, doublets from the equivalent C_3 and C_8 protons, and the equivalent C_5 and C_6 protons, and a triplet arising from the equivalent C_4 and C_7 protons, would be expected. Two sets of doublets at δ 8.75 ppm (two protons, J = 8 Hz) and 8.90 (two protons, J = 8 Hz), and a triplet at δ 8.15 (two protons, J = 8) are observed in the pmr spectrum at coalescence temperature (+40°).

The temperature dependence of the pmr spectrum of ion **2a** could also be interpreted in terms of a nonclassical bridged structure such as **15**. However, it is more likely that ion **15** is only a transition state in the



15

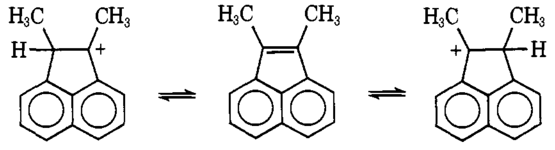


16

1,2-hydrogen shift process rather than a stable intermediate. The slow rate of the 1,2-hydrogen shift in 1,2-dimethyl-1-acenaphthenium ion compared with that of the extremely fast process observed in the acyclic equilibrating dimethylisopropylcarbenium ion, which does not have the nonclassical bridged structure **16**, suggests that the bridged structure **15** for a more rigid acenaphthene system is even less likely. Additional evidence against a bridged structure is also indicated by the stereochemical course (cis) of the addition reaction of HX or X_2 (X = Cl or Br) to acenaphthylene.[18,19] In this case a classical carbenium ion, paired with a X^- ion, is probably formed, and this ion pair collapses to give predominantly cis addition. If the bridged intermediate was formed mostly trans product would be observed.

Other mechanisms, involving intramolecular rearrangements more complex than simple 1,2-hydrogen shifts, appear unlikely, since a highly strained four-membered ring intermediate (or transition state) would need to be invoked.[11b]

Proton exchange with the solvent is observed as a secondary process, along with the rapid 1,2-hydrogen shift, when a solution of **2a** is warmed above +50°. At +80°, only a sharp singlet for the six methyl protons is observed at δ 2.75 ppm in the pmr spectrum (Figure 2). There is no change in the aromatic proton signals. The observed spectral changes in the temperature range, 40–80°, are completely reversible, and are consistent with the following process.



One must consider the possibility of a rapid intramolecular 1,2-methyl shift process at elevated temperature. However, this does not seem to be the case from the pmr spectral data. If an intramolecular 1,2-methyl shift does take place (pathway b), the methyl group chemical shift should appear at about δ 2 ppm or even

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(18) (a) R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1965, pp 123, 125; (b) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2245 (1963); (c) F. D. Greene, W. A. Remers, and J. W. Wilson, *ibid.*, **79**, 1416 (1957).

(19) P. B. D. de la Mare and N. V. Klassen, *Chem. Ind.* (*London*), 498 (1960).

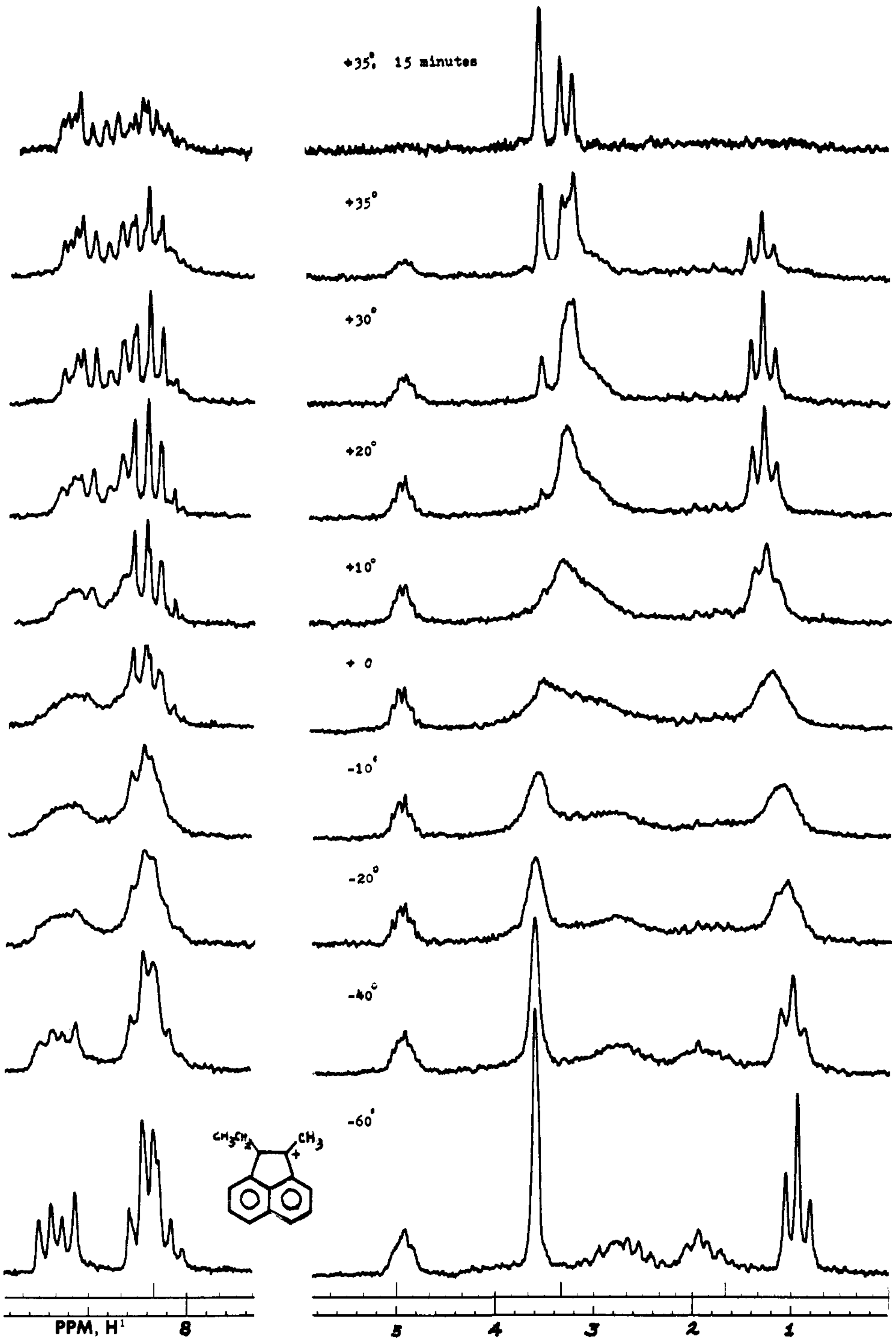
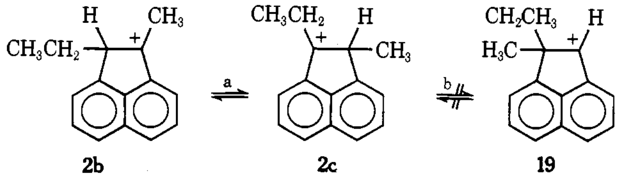


Figure 3. The 60-MHz pmr spectra of 1-methyl-2-ethyl- and 2-methyl-1-ethyl-1-acenaphthenium ions.

at a higher field. The observed value, however, is 2.75 ppm (*vide supra*). Additional evidence for the above proton exchange process is indicated by the deuterium incorporation which occurs at the C_1 and C_2 positions (*ca.* 35% incorporation after 2 min at +60°) when the ion **2a** is warmed in a $FSO_3H-D_2SO_4-SO_2ClF$ solution.

The cmr spectrum of the 1,2-dimethyl-1-acenaphthenium ion (**2a**) at −60° shows similar features to those of ion **1b**. The carbon chemical shift of the carbenium center is found at $\delta_{^{13}C}$ −29.7, which is only 7 ppm shielded from that of ion **1b** ($\delta_{^{13}C}$ −36.7). This also confirms the classical nature of ion **1b**. At temperatures when equilibration takes place, the cmr spectrum of ion **2a** was not obtainable because the ion decomposed before a sufficient number of free induction decay signals were accumulated.

F. 1-Methyl-2-ethyl- and 2-Methyl-1-ethyl-1-acenaphthenium Ions (2b and 2c). 1-Methyl-2-ethyl-1-acenaphthenium ion (**2b**) was generated from 1-ethyl-2-methyl-1-acenaphthenol (**18**) in either FSO_3H-SO_2ClF or $FSO_3H-SbF_5-SO_2ClF$ solutions at −78° through the rearrangement of the unstable 2-methyl-1-ethyl-1-acenaphthenium cation (**2c**). The observed temperature dependence of the pmr spectrum of ion **2b** (Figure 3) is similar to that shown by ion **2a**, and indicates a pair of rapidly equilibrating ions (**2b** ⇌ **2c**) between

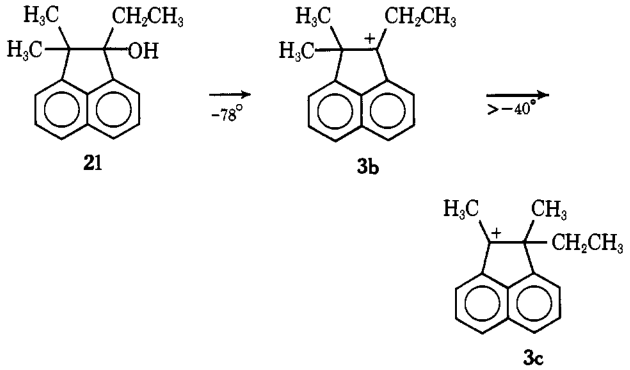


-50 and $+25°$. As for ion **2a**, there is no evidence for intramolecular 1,2-alkyl shifts (path b). The reason ion **2b** is more stable than ion **2c** at $-60°$ may be due to steric factors, or it may be that the methyl group is superior to the ethyl group, in this molecule at least, at accommodating positive charge on an adjacent carbon atom.

The solution of the equilibrating ions **2b** ⇌ **2c** is not stable at temperatures above $+25°$, and gradually undergoes irreversible conversion to an unknown cation, whose structure is under further examination (Figure 3).

G. 1,2,2-Trimethyl-1-acenaphthenium ion (3a) is prepared from the ionization of 1,2,2-trimethyl-1-acenaphthenol (**20**) in either FSO_3H, FSO_3H-SbF_5 (1:1), or SbF_5 diluted with SO_2ClF at $-78°$. Surprisingly, ion **3a** is shown to be a static nonequilibrating ion with no evidence of an intramolecular 1,2-methyl shift in the temperature range studied (-78 to $+170°$). The pmr spectrum (60 MHz) is found to be only slightly broadened at $+170°$. Since both the dimethyl-*tert*-butylcarbenium[8] and the 9,10,10-trimethylphenanthrenium[11a] cations have been reported as pairs of rapidly equilibrating ions involving fast intramolecular 1,2-methyl shifts, the absence of a similar rearrangement in ion **3a** can only be explained as a result of its more rigid molecular geometry. According to models, slight movement of a methyl group toward a position where it could migrate to the adjacent carbon atom causes a large amount of strain within the molecule. It would appear that the tertiary–tertiary intramolecular 1,2-methyl shift process in ion **3a** should be less facile than that of the corresponding 1,2-hydrogen shift in ion **2a**. In the latter case, when the hydrogen starts to equilibrate, the steric repulsion between the two methyl groups can be slightly released as the ion assumes the geometry of the transition state. In ion **3a**, however, the methyl migration does not release the severe steric strain existing between the three bulky methyl groups. In the trimethylphenanthrenium ion, the six-membered ring is able to be twisted in the transition state so that there is a release of the steric repulsion among the methyl groups. The rigid five-membered ring in the trimethylacenaphthenium ion molecule, however, is incapable of undergoing a similar deformation. That there is some hindrance to methyl migration in the 9,10,10-trimethylphenanthenium ion,[11] is indicated by the fact that a much higher temperature ($+18°$) is required for it to equilibrate than is needed for equilibration to occur in the dimethyl-*tert*-butylcarbenium ion (at least lower than $-60°$).

H. 2,2-Dimethyl-1-ethyl- and 1,2-Dimethyl-2-ethyl-1-acenaphthenium Ions (3b and 3c). 2,2-Dimethyl-1-ethyl-1-acenaphthenium ion (**3b**) can be generated from the alcohol **21** in FSO_3H or FSO_3H-SbF_5 solutions diluted with $SO_2ClF(SO_2)$ below $-60°$. The 60-MHz pmr spectrum of ion **3b** consists of a sharp singlet at δ 1.90 (six protons), a triplet centered at δ 1.90 (three protons, $J = 7.0$ Hz), a quartet centered at δ 3.82 (two protons, $J = 7$ Hz), an aromatic multiplet extending from δ 8.1 to 8.5 (four protons), and two sets of doublets centered at δ 9.2 (one proton, $J = 8$ Hz) and 9.35 (one proton, $J = 7$ Hz). Ion **3b** is formed quickly, and irreversibly rearranges to ion **3c** on warming to $-40°$. At $-30°$, the pmr spectrum of the solution indicates that it is entirely ion **3c**. A similar rearrangement occurs at much lower temperature for the 2-methyl-1-ethyl-1-acenaphthenium ion **2c**, and this has been discussed in an earlier section.



The 60-MHz pmr spectrum of ion **3c** consists of a triplet at δ 0.60 (three protons, $J = 7.6$ Hz), a quartet at δ 2.60 (two protons, $J = 7.6$ Hz), two sharp singlets at δ 1.90 (three protons) and 3.50 (three protons), an aromatic multiplet centered at δ 8.2–8.6 (four protons) and two sets of doublets centered at δ 9.2 (one proton, $J = 8$ Hz) and 9.55 (one proton, $J = 7$ Hz). When the solution of **3c** is warmed to $+50°$, all the pmr signals are broadened and at $+80°$ only a single broad peak is observed. However, on further warming to $+95°$, a new species forms and at 110° the solution consists entirely of this ion. The pmr spectrum of the last species consists of two sharp singlets at δ 2.80 (three protons) and 3.35 (six protons), a triplet centered at δ 8.40 (two protons, $J = 8.0$ Hz), and two sets of doublets at δ 9.18 (two protons, $J = 8.0$ Hz) and 9.60 (two protons, $J = 8$ Hz). The available evidence seems to indicate that the ion is the 1,2,3-trimethyl-1-perinaphthenylium cation (**22**). Even though the parent perinaphthenylium cation has been prepared as a stable salt, no pmr data are available. Perinaphthenylium cations have been found of theoretical interest. Efforts directed toward understanding their structures are being made using pmr and cmr spectroscopy.

The mechanism for the formation of **22** from ions **3b** and **3c** can be rationalized as in Scheme I. Although ion **3c** is the major species at temperatures above $-40°$, there may also be present a small amount of ion **3b**. Ion **3b** can undergo a 1,2-hydrogen shift and ring expansion to give either **24** or **25**. The latter, once formed, will undergo a methyl shift to form **26**, which in turn can lose two hydrogen atoms at high temperature to give **22**. The latter process is not unusual since several simple alcohols are known to give allylic type ions.[20]

Experimental Section

Proton Nuclear Magnetic Resonance Spectroscopy. Proton nuclear magnetic resonance spectra were obtained with a Varian Associates Model A56/60A nmr spectrometer equipped with a

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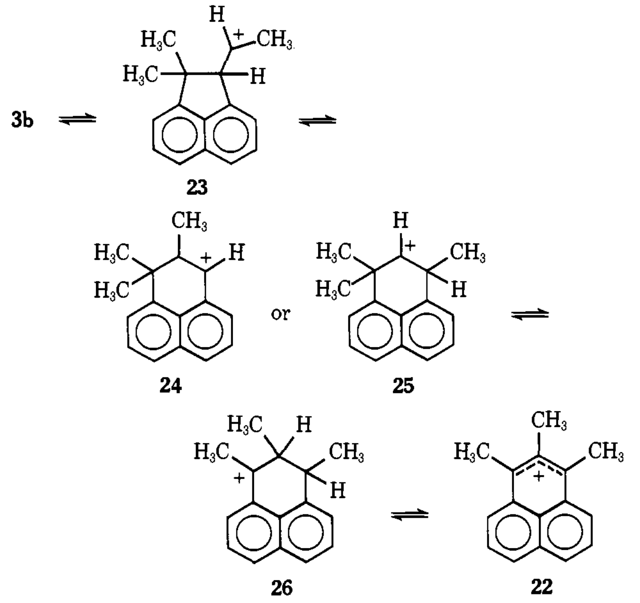
[20] N.C. Deno, ref 6a, Chapter 18.

Scheme I



variable-temperature probe. External TMS (capillary tube) was used as reference. Pressure nmr tubes were used for high-temperature nmr measurements.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Cmr spectra were obtained on a Varian Associates Model HA-100 spectrometer equipped with a FT-100 Fourier transform accessory (V-4357 Pulsing and Control unit), a broad band proton decoupler (V-3512), and a variable-temperature probe.

A pulsed frequency of 25.14 MHz was derived from a gated power amplifier capable of putting out approximately 80 W into the transmitter coils. The pulse width used was 30 μsec and the pulse interval, 1.7 sec. The available computer memory (4000 input channels) and the need to provide multichannel excitation over the region of interest (sweep width = 6500 Hz) limited the data acquisition time to 0.3 sec.

The free induction signal derived after each pulse was digitized and accumulated in a Varian 620/i Computer (8K). Approximately 3000–4000 accumulations were made for each spectrum. Field/frequency regulation was maintained by the spectrometer's homonuclear internal lock system. The lock used was the proton decoupled ^{13}C resonance of a 60% ^{13}C-labeled methyl iodide sample contained in a precision coaxially spaced capillary (o.d. approximately 0.2 and 0.4 mm) inserted in the sample nmr tube (5 mm o.d.).

Fourier transformation of the accumulated free induction signal gave the frequency spectrum,[21] from which was measured the chemical shift of each signal, relative to the reference methyl iodide signal. All the chemical shifts reported here have been corrected to a carbon disulfide reference, by the relationship

$$\delta_{CS_2}\,(\text{ppm}) = 212.2 - a\delta T - \delta_{CH_3I}\,(\text{ppm})$$

where δ_{CS_2} and δ_{CH_3I} are the chemical shifts in parts per million of a particular signal, from carbon disulfide and methyl iodide, respectively. The term $a\delta T$ allows for the observed temperature variation in the chemical shift of internal carbon disulfide with respect to that of external methyl iodide, δT is the difference between the normal probe temperature (30–35°) and the temperature at which a spectrum is recorded. A plot of sample temperature *vs.* the ^{13}C chemical shift difference between external methyl iodide and carbon disulfide is linear with a slope of $a = 0.029 \pm 0.002$ ppm/deg. The slope was found to be almost identical for several carbon disulfide–cosolvent systems, so the above expression is most likely valid for the superacid solvent systems used in this study.

Preparation of Ions. Twice distilled FSO_3H, freshly prepared FSO_3H–SbF_5 (1:1), and saturated solutions of SbF_5 in SO_2ClF, respectively, were cooled to −78° with a Dry Ice–acetone bath. To the appropriate acid solution was slowly added, with vigorous stirring, a cold solution of the acenaphthene precursors in SO_2ClF in an amount to give an approximately 15% solution of the ion. The solution was then transferred to a precooled nmr tube. In general, all the acenaphthenium cation solutions were a dark-wine or deep red color.

1-Acenaphthenol (2) was purchased from Aldrich Chemical Co. and used without purification.

1-Methyl-1-acenaphthenol (5), 2-methyl-1-acenaphthenol (6), 1-acenaphthenone-(9) ***cis-*** **and** ***trans*****-1,2-dimethyl-1-acenaphthenol (12), 2,2-dimethyl-1-acenaphthenol (14), and 1,2,2,-trimethyl-1-acenaphthenol (20)** were prepared according to published procedures.[22]

1-Ethyl-1-acenaphthenol (8) was prepared in 95% yield from **9** with ethylmagnesium bromide in the usual fashion: mp 105–106° (petroleum ether, bp 30–60°); nmr (external TMS, $CDCl_3$) δ 1.5 (t, J = 7 Hz, 3 H), 3.6 (q, J = 7 Hz, 2 H), 3.90 (s, 2 H), 7.5–8.2 (m, 6 H), and 2.5 (s, 1 H).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.84; H, 7.07. Found: C, 84.59; H, 7.21.

cis- **and** ***trans*****-2-methyl-1-ethyl-1-acenaphthenol (18)** were prepared in 80% yield from 2-methyl-1-acenaphthenone[22a] and ethylmagnesium bromide: mp 85–98° (pentane); nmr (external TMS, $CDCl_3$) δ 1.46 (t, J = 7 Hz, 3 H), 1.90 (d, J = 7.2 Hz, 3 H), 2.5 (q, J = 7.0 Hz, 2 H), 2.68 (s, 1 H), 4.05 (2, J = 7 Hz, 1 H), and 8.6–9.3 (m, 6 H).

1-Ethyl-2,2-dimethyl-1-acenaphthenol (21) was prepared from 2,2-dimethyl-1-acenaphthenone,[22a] in the same way as **18**, mp 104–105°. The carbinol was stored in the refrigerator because it slowly decomposed upon standing at room temperature. Its nmr spectrum in $CDCl_3$ (external TMS) showed one hydroxy proton singlet at δ 1.9, two different methyl groups at δ 2.32 and 2.42, and a methyl triplet at δ 1.0 (J = 7.2 Hz), a methylene multiplet centered at δ 1.9 and aromatic protons at 8.1–8.8 in the ratio 1:3:3:3:2:6. This spectrum is consistent with the assigned structure. *Anal.* Calcd for $C_{16}H_{18}O$: C, 84.96; H, 7.96. Found: C, 84.43: H, 8.01.

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(21) (a) R. R. Ernst, *Advan. Magn. Resonance*, **2**, 74 (1966); (b) A. Abragam, "Principles of Magnetic Resonance," Oxford University Press, London, 1961, p 114; (c) R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, 37, 93 (1966).

(22) (a) A. Bosch and R. K. Brown, *Can. J. Chem.*, **46**, 715 (1968); (b) P. W. Westerman, Ph.D. Thesis, The University of Sydney, 1970.