molecules. Final atomic parameters are listed in Table II, and selected structural parameters are listed in Table III, with the less reliable values for the primed molecule in parentheses. A stereoview of the unprimed molecule is shown in Figure 2.

Acknowledgment. We thank the National Science Foundation (CHE-8009670) for support of this work.

Registry No. Bis(9-triptycyl) ketone, 82510-94-9; bis(9-triptycyl)-methane, 73611-46-8.

Supplementary Material Available: Structure factor tables, final anisotropic thermal parameters, atomic parameters for hydrogen and solvent atoms, bond lengths, and bond angles with standard deviations for Tp_2CO and Tp_2CH_2 (Tables IV–XIII) (49 pages). Ordering information is given on any current masthead page.

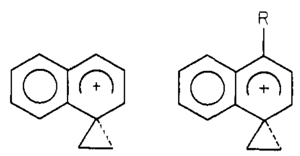
Stable Carbocations. 209.[1] α-Ethylenenaphthalenium Ions

George A. Olah* and Brij P. Singh

Contribution from the Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90007. *Received January 8, 1982*

Abstract: Ionization of 2-α-naphthylethyl chloride (**5**) and 2-β-naphthylethyl chloride (**9**) in FSO_3H–SbF_5/SO_2ClF at −80 °C gave the protonated naphthalenium ions **6** and **10** or the rearranged naphthylethyl cation **8**, which were observed by carbon-13 and proton NMR spectroscopy. Spiro alcohol **12a** under similar conditions gave only polymeric material. The 4-methyl-substituted precursor **13a** on ionization gave the corresponding 4-methyl-substituted α-ethylenenaphthalenium ion **2** and a minor amount of ion **14**. Ionization of phenyl-substituted spirocyclic tertiary alcohol **17** gave the corresponding ion **18**. Protonation and methylation of the spiro ketone **12** led us to observe the spirocyclic ions **21** and **22** whose structures were proved by carbon-13 and proton NMR spectroscopy.

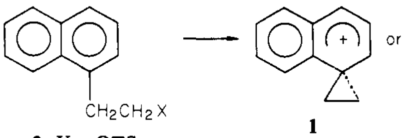
In continuation of our studies on the nature of phenylethyl cations,[2] we now wish to report efforts to prepare the elusive α-ethylenenaphthalenium ion **1** and the first direct observation



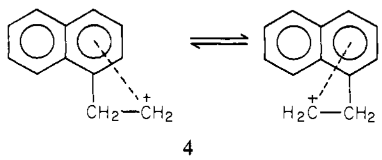
1 **2**

R = CH_3, C_6H_5, OH, OCH_3

of its substituted homologues, that of the 4-methyl-, 4-phenyl-, 4-hydroxy-, and 4-methoxy-α-ethylenenaphthalenium ions **2**, under stable ion conditions. Participation by the naphthyl group has been proposed in solvolytic studies[3a–d] of 2-α-naphthylethyl derivatives **3**. The results were interpreted in terms of α-ethylenenaphthalenium ion **1** or a rapidly equilibrating pair of π-bridged ions[3e] such as **4** intermediates.



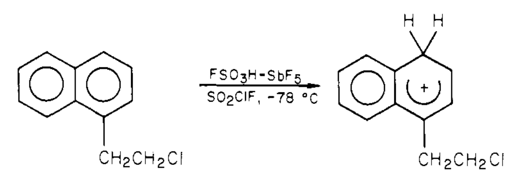
3, X = OTS **1**



4

Results and Discussion

In our efforts to prepare ion **1**, we added 2-α-naphthylethyl chloride (**5**) in SO_2ClF to a well-stirred solution of FSO_3H–



5 **6**

SbF_5/SO_2ClF at −78 °C, resulting in a brownish yellow solution. The 60-MHz proton NMR spectrum of this solution at −80 °C displayed absorptions at δ 4.25 (s, 4 H), 5.2 (br s, 2 H), 8.4 (m, 4 H), 8.96 (d, 1 H), and 9.53 (d, 1 H). Observation of a total of 12 protons in the spectrum shows that under the superacidic conditions protonation has taken place on the ring. The 20-MHz carbon-13 NMR spectrum of the solution displayed three absorptions in the aliphatic region, at $\delta_{^{13}C}$ 39.6 (t), 43.0 (t), and 44.2 (t), and nine more peaks in the aromatic and also low-field region. The observation of three saturated methylene groups in the proton and carbon-13 NMR spectra clearly rules out structure **1**. If the spectrum were that of the parent ion **1**, it should show only two peaks in the aliphatic region of the carbon-13 NMR spectrum, one for the symmetrical cyclopropane methylenes and the other for the spiro quaternary carbon atom. The presence of three triplets in the aliphatic region of the proton-coupled carbon-13 NMR spectrum indicates ring protonation, i.e., the 4-(β-chloroethyl)-1-naphthalenium ion **6**. Indeed, the proton and carbon-13 NMR chemical shifts of the observed ion **6** (Table II) are comparable to those of the previously reported[4] 1-methylnaphthalenium ion **7**. Even after being warmed to −50 °C, ion **6** was found to be stable, with no indication of the formation of ion **1**. On the other hand, when 2-α-naphthylethyl chloride (**5**) was ionized in SbF_5/SO_2ClF alone at −78 °C, it gave the α-

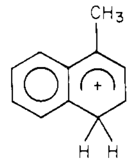
(1) Part 208: Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026.

(2) (a) For discussion concerning the nomenclature of ethylenebenzenium ions, see: Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808; *Chimia* **1971**, *8*, 275; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173. (b) For recent reviews, see: Schleyer, P. v. R.; Lancelot, C. J.; Cram, D. J. "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1969; Vol. III. Story, P. R.; Clark, B. C., Jr. *Ibid.* Chapter 23. (c) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 2236; **1976**, *98*, 6304. (d) Olah, G. A.; Porter, R. D. *Ibid.* **1971**, *93*, 6877; **1970**, *92*, 7627. (e) Olah, G. A.; Comisarow, M. B.; Kim, C. J. *Ibid.* **1969**, *91*, 1458. (f) Olah, G. A.; Pittman, C. U., Jr. *Ibid.* **1965**, *87*, 3507.

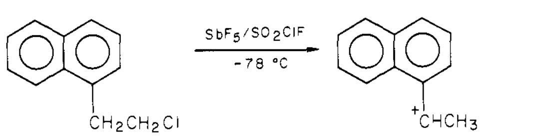
(3) (a) Eberson, L.; Petrovich, J. P.; Baird, R.; Dyckes, D.; Winstein, S. *J. Am. Chem. Soc.* **1965**, *87*, 3504. (b) Bentley, M. D.; Dewar, M. J. S. *Ibid.* **1968**, *90*, 1075; **1970**, *92*, 3991. (c) Lee, C. C.; Framan, A. G. *Can. J. Chem.* **1965**, *43*, 3386. (d) Cram, D. J.; Daton, C. K. *J. Am. Chem. Soc.* **1963**, *85*, 1268. (e) Brown, H. C.; Morgan, K. J.; Chloupek, F. J. *Ibid.* **1965**, *87*, 237.

(4) Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299.

0002-7863/82/1504-5168$01.25/0



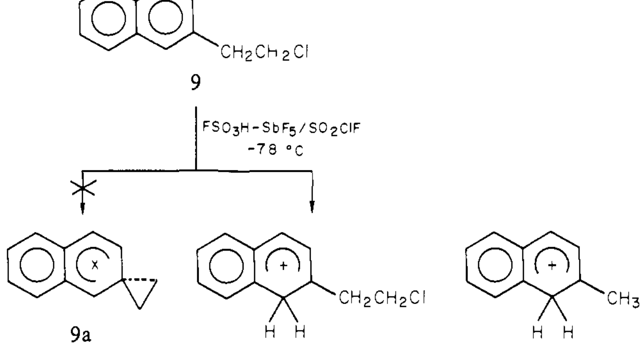
7



5 8

naphthylethyl cation **8**, an open-chain rearranged ion formed after a hydride shift. The structure of this ion was confirmed by comparing its carbon-13 and proton NMR spectra with those reported earlier.[5]

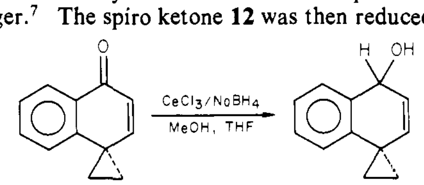
Similarly, the ionization of 2-β-naphthylethyl chloride (**9**) in



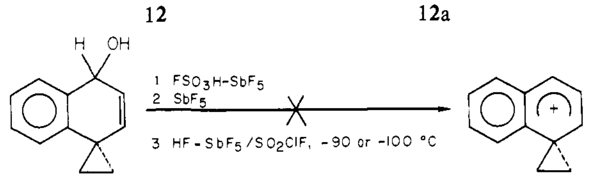
9 9a 10 11

FSO_3H-SbF_5 in SO_2ClF solution at −78 °C did not form the expected ion **9a**, reported earlier in the solvolytic studies.[6] However, the carbon-13 and proton NMR spectra of the above ion proved it to be the 2-(β-chloroethyl)naphthalenium ion **10**. The NMR chemical shifts of ion **10** were found comparable to those of reported protonated 2-methylnaphthalenium ion **11**[4] (Table II). In both cases starting from precursors **5** or **9**, we were unable to prepare the parent ion **1** or **9a**.

We also tried to prepare ion **1** by ionizing another precursor alcohol, **12a**. For the preparation of this alcohol, we first prepared the spiro ketone **12** by a series of reactions reported by Rys and Vogelsanger.[7] The spiro ketone **12** was then reduced to alcohol



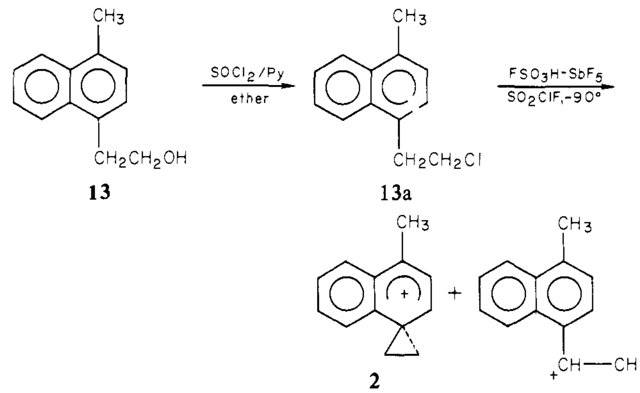
12 12a



12a 1

12a by the specific method of Luche[8] (see Experimental Section). Our attempts to prepare ion **1** by the ionization of spirocyclic secondary alcohol **12a** under a variety of superacidic conditions were unsuccessful and resulted only in polymeric materials.

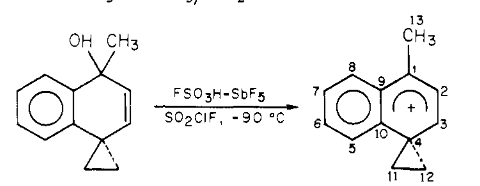
Since methyl substitution is known to stabilize carbenium ions, next we prepared the 4-methyl-substituted precursor **13a** from alcohol **13**, and its ionization was studied. When a slurry of **13a** in SO_2ClF was added to a well-stirred solution of FSO_3H–SbF_5/SO_2ClF at −90 °C, a brownish yellow solution was obtained.



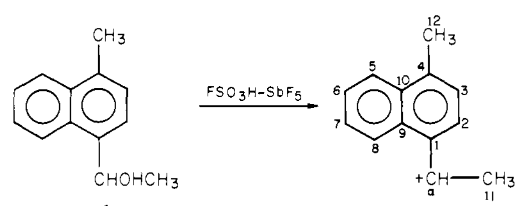
13 13a 2 14

The carbon-13 and proton NMR spectra of this solution showed it to be the elusive 4-methyl-α-ethylenenaphthalenium ion **2** with a minor amount of ion **14** also present (Figure 1a). The relative concentrations of ions **2** annd **14** did not change even upon warming the ion solution to −50 °C. The same relative ratios of ions **2** and **14** were obtained even when the ionization was carried out at −110 °C. The structures of ions **2** and **14** were proved by their independent preparations.

A slurry of spirocyclic tertiary alcohol **15** in SO_2ClF was ionized in a solution of FSO_3H-SbF_5/SO_2ClF at −90 °C. The 200-MHz



15 2



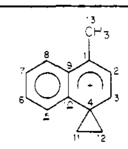
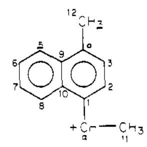
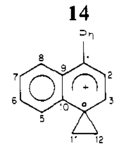
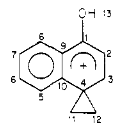
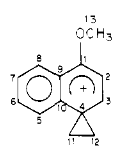
16 14

proton NMR spectrum of this solution displayed absorptions at δ 2.57 (s, 3 H), 3.37 (s, 4 H), 7.12 (d, 1 H), 7.3 (t, 1 H), 7.4 (d, 1 H), 7.52 (t, 1 H), 7.88 (d, 1 H), and 7.93 (d, 1 H), for a total of 11 protons (Table I). The carbon-13 NMR spectrum of the solution at −90 °C (Figure 1b) displayed three peaks, at $\delta_{^{13}C}$ 22.57 (q, CH_3 group), 48.47 (t, symmetrical methylenes of cyclopropane ring), and 52.57 (s, aliphatic spiro quaternary carbon atom), and nine other peaks (Table II) assigned as follows: C_3, 180.39 (d); C_1, 178.12 (s); C_{10}, 151.96 (s); C_6, 137.30 (d); C_9, 132.98 (s); C_2, 132.31 (d); C_8, 130.25 (d); C_7, 128.16 (d); and C_5, 121.55 (d). Assignments of all the proton and carbon-13 resonances in this ion as well as in others were based on the reported naphthalenium ions.[4,9,10] The most deshielded resonances were assigned to the carbons and protons that are in conjugation to the carbonium ion center. Upon heating the above ion solution to −50 °C, we observed no change in the carbon-13 NMR spectrum. However, further heating above −50 °C resulted in decomposition without a trace of any open-chain ion **14**.

Similarly, ion **14** was independently prepared by ionizing **16** under stable ion conditions at −90 °C. The 200-MHz proton

(5) Olah, G. A.; Forsyth, D. A.; Spear, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 2512.
(6) Lee, C. C.; Forman, A. G. *Can. J. Chem.* **1966**, *44*, 841.
(7) Rys, von P.; Vogelsanger, R. *Helv. Chim. Acta.* **1972**, *55*, 2844.
(8) Luche, J. L.; Hahn, L. R.; Crabbe, P. *J. Chem. Soc., Chem. Commun.* **1978**, 601.
(9) Olah, G. A.; Mateescu, G. D.; Mo, Y. K. *J. Am. Chem. Soc.* **1973**, *95*, 1865.
(10) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1979**, *101*, 3618.

Table I. Proton NMR Parameters of α-Ethylenenaphthalenium Ions[a]

ions	proton chemical shifts and multiplicities									
	H_2	H_3	H_5	H_6	H_7	H_8	H_{11}	H_{12}	H_{13}	H_α
 **2**	7.4[b] (d)	7.93 (d)	7.12 (d)	7.52 (t)	7.3 (t)	7.88[b] (d)	3.4 (s)	3.4 (s)	2.6 (s)	
 **14**	8.4 (d)	7.83 (d)	7.9 (d)	7.32 (t)	7.53 (t)	7.28 (d)	2.42 (d)	2.53 (s)		9.2 (q)
 **18**	7.7 (m)	8.2 (d)	7.4 (d)	7.7 (m)	7.7 (m)	8.0 (d)	3.7 (d)	3.7 (d)		
 **21**	7.05[b] (d)	8.1 (d)	6.9 (d)	7.6 (t)	7.3 (t)	7.65[b] (d)	2.7 (s)	2.7 (s)	9.7 (s)	
 **22**	7.3[b] (d)	8.2 (d)	7.2 (d)	7.8 (t)	7.5 (t)	7.9[b] (d)	2.9 (d)	2.9 (d)	4.0 (b m)	

[a] s = singlet, d = doublet, t = triplet, m = multiplet, and b = broad. Phenyl protons of ion 18 showed singlet at δ 7.3. [b] Assignments are interchangeable.

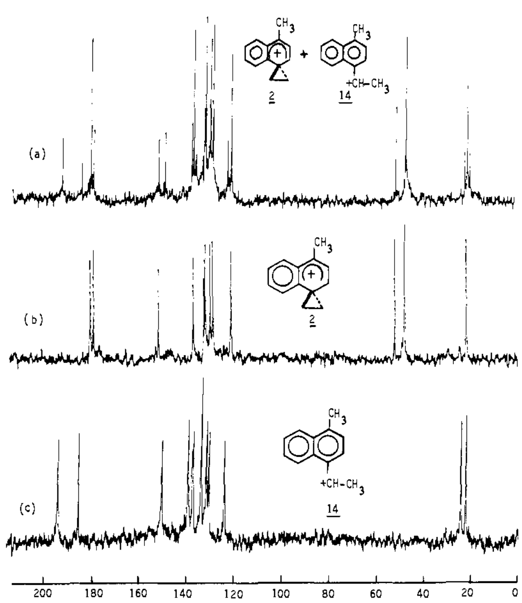
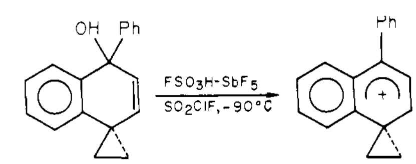


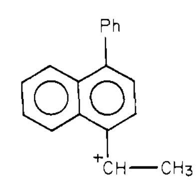
Figure 1. Carbon-13 NMR spectra of ions **2** and **14**.

NMR spectrum of the brownish yellow solution displayed a highly deshielded quartet at δ 9.2 for the proton at the positively charged carbon, a doublet at 8.39 (1 H, C_2), a doublet at 7.91 (1 H, C_5), a doublet at 7.83 (1 H, C_3), a triplet at 7.53 (1 H, C_7), a triplet at 7.32 (1 H, C_6), a doublet at 7.28 (1 H, C_8), a sharp singlet at 2.53 (3 H, aromatic methyl), and a doublet at 2.42 (3 H, side-chain methyl). The carbon-13 NMR spectrum, Figure 1c, at −80 °C displayed peaks at $\delta_{^{13}C}$ 21.76 and 23.83 for the two methyl groups. The lowest field peak at 192.73 was assigned to the carbon bearing positive charge. The rest of the peaks were assigned (Table II) as follows: C_4 (184.32, s), C_2 (138.44, d), C_9 (136.81, s), C_1 (136.42, s), C_5 and C_{10} (133.09), C_6 (130.81, d), C_3 (129.73, d), and C_8 (123.24, d). This ion was also found to be stable up to −50 °C.

In search of further substituted ions, we have also observed the 4-phenyl-α-ethylenenaphthalenium ion **18** by ionizing precursor **17** in FSO_3H-SbF_5/SO_2ClF at −90 °C. The carbon-13 NMR



17 **18**

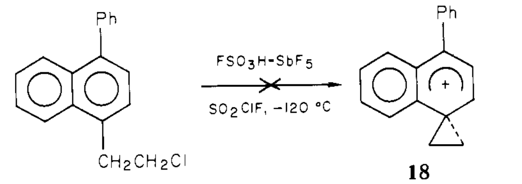


19

spectrum showed peaks at $\delta_{^{13}C}$ 53.65 (s, aliphatic spiro quaternary carbon) and 50.69 (t, symmetrical cyclopropane methylenes). The low-field peaks at 179.65 (d), 175.89 (s), and 154.35 (s) were assigned to C_3, C_1, and C_{10} of ion **18**. The rest of the peaks in the olefinic region were assigned satisfactorily to the rest of the carbons (Table II). As the ion solution was warmed to −70 °C, it polymerized without the observation of the open-chain ion **19**.

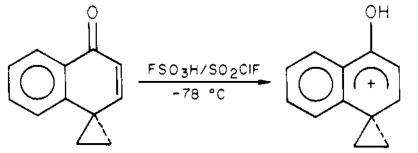
The proton NMR spectrum of ion **18** even at −90 °C is not entirely clean but showed absorptions at δ 3.7 (s), 7.3 (s), 7.4 (d), 7.7 (m), 8.0 (d), and 8.2 (d) that are, however, assignable to the protons in ion **18** (Table I).

Our efforts to prepare ion **18** independently from another precursor **20** were unsuccessful. When **20** was ionized even at −120 °C, only polymeric products were formed.

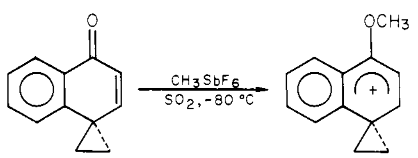


20　**18**

We have, however, succeeded in obtaining 4-hydroxy- and 4-methoxy-α-ethylenenaphthalenium ions **21** and **22** by protonation as well as methylation of spiro ketone **12**.



21



12　**22**

Upon slow addition of spiro ketone **12** to a well-stirred solution of FSO_3H/SO_2ClF at −78 °C, a brownish green solution of ion **21** was obtained. The proton NMR spectrum of this ion at −78 °C displayed a sharp singlet at δ 2.7 (methylene protons of cyclopropane ring), a sharp singlet at 9.7 (probably due to the hydroxy proton), and a doublet at 8.1 (proton at C_3). The additional peaks were satisfactorily assigned to the rest of the ring protons in ion **21** (Table I). The carbon-13 NMR spectrum shows two peaks in the aliphatic region, one at $\delta_{^{13}C}$ 37.5, symmetrical methylenes of cyclopropane ring, and another at $\delta_{^{13}C}$ 40.5 for the aliphatic spiro quaternary carbon atom. The low-field peaks at $\delta_{^{13}C}$ 182.8, 178.8, and 150.0 were assigned to C_1, C_3, and C_{10} of ion **21**, respectively. The additional six peaks were assigned to remaining carbon atoms as shown in Table II.

When the spiro ketone **12** was slowly added to a well-stirred solution of $CH_3F/SbF_5/SO_2/SO_2ClF$ at −80 °C, a brownish yellow solution was obtained. The proton NMR spectrum of methylated ion **22** at −80 °C displayed absorptions at δ 2.9 (s, 4 H), 4.0 (br m, 3 H), 7.2 (d, 1 H), 7.3 (d, 1 H), 7.5 (t, 1 H), 7.8 (t, 1 H), 7.9 (d, 1 H), and 8.2 (d, 1 H), which were satisfactorily assigned for ion **22** as shown in Table I. The carbon-13 NMR showed 12 peaks with assignments given in Table II. Both ions **21** and **22** are stable up to −50 °C, above which temperature they start decomposing.

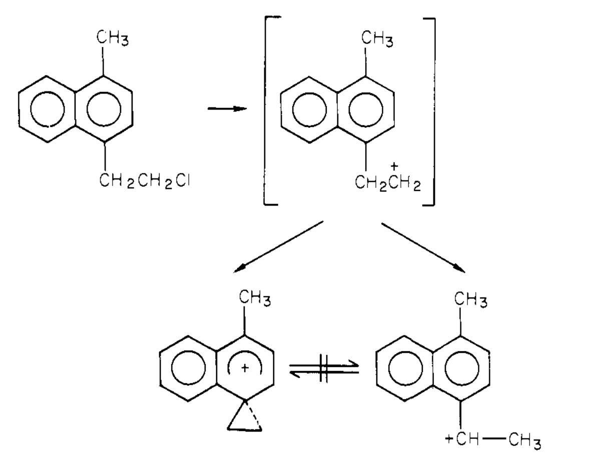
Conclusions

In the present study the methyl-substituted α-ethylenenaphthalenium ion has been observed upon ionization of α-naphthylethyl precursor **13a**, as well as independently prepared from appropriate spirocyclopropyl alcohol **15**. The ratio of ions **2** and **14** obtained from precursor **13a** does not change even upon heating the ion solution to −50 °C, which proves that they are not in equilibrium.

Also, a number of other substituted α-ethylenenaphthalenium ions such as **18**, **21**, and **22** from different precursors have been observed. The present study is the first example in which participation of the naphthyl group in ionization of α-naphthylethyl precursor **13a** is observed under stable ion conditions. These results support previous conclusions reached in solvolytic studies on the involvement of these ions as reaction intermediates.

Experimental Section

All the boiling and melting points are uncorrected. All proton spectra of starting materials and ions, unless specified, were recorded on Varian



XL-200 superconducting NMR spectrometer. All the carbon-13 spectra were recorded on a Varian FT-80 NMR spectrometer equipped with a multinuclear broad-band probe and variable-temperature controller. All the compounds used in this study were prepared in the laboratory except 1-bromo-4-methylanphthalene, 4-bromoanisole, 1-naphthaleneethanol, and 2-naphthaleneethanol, which were obtained from Aldrich Chemical Co. All proton and carbon-13 NMR chemical shifts are referenced to external tetramethylsilane.

2-α-Naphthylethyl Chloride (5). To a solution of 1-naphthaleneethanol (10 g, 58.06 mmol) and 2 mL of, dry pyridine in 100 mL of, dry ether was slowly added 20 mL of, thionyl chloride. The resulting solution was refluxed overnight. The cold reaction mixture was poured into ice water, extracted with ether, washed with dilute HCl and water, and dried. Evaporation of solvent yielded chloride **5** (10 g, 90.3%): bp 90 °C (0.25 mm); ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.6–4.2 (4 H, m), 7.6–8.4 (7 H, m).

2-β-Naphthylethyl Chloride (9). A mixture of 2-naphthaleneethanol (15 g, 87.09 mmol), 4 mL of dry pyridine in 120 mL of dry ether, and 30 mL of thionyl chloride was refluxed overnight. The cold solution was poured into ice water, extracted with 2 × 150 mL of ether, washed with dilute HCl and water, and dried over anhydrous $MgSO_4$. Evaporation of ether gave (16 g, 83.9%) a white solid: mp 52.3 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.35 (2 H, t), 3.95 (2 H, t), 7.4–8.3 (7 H, m).

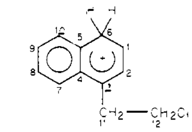
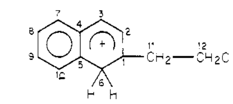
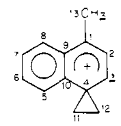
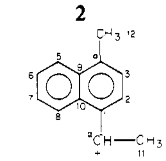
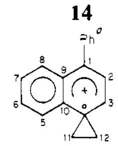
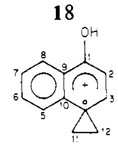
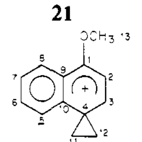
Benzo[*a*]spiro[2.5]octa-1,4-dien-3-ol (12a). To a solution of ketone **12** (5 g, 29.4 mmol) and anhydrous $CeCl_3$ (7.5 g, 30.4 mmol) in 100 mL of methanol and 50 mL of THF at ice temperature was added $NaBH_4$ (1.15 g, 30.4 mmol) in portions within 5 min. The reaction mixture was stirred an additional 10 min. It was quenched with cold water, extracted with ether, washed, and dried. Evaporation of solvent gave 5 g of low-melting solid: ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.0–1.3 (4 H, br d), 3.15 (1 H, d), 5.2 (1 H, d), 5.9 (1 H, dd), 6.6 (1 H, m), 7.2 (2 H, d), 7.5 (1 H, m); ^{13}C NMR (ppm, $CDCl_3$) 20.3, 20.57, 21.21, 65.83, 120.9, 123.1, 125.4, 126.0, 126.75, 128.1, 129.4, 135.9.

1-Methyl-4-(2-hydroxyethyl)naphthalene (13). To a 500-mL three-necked flask containing magnesium metal (2 g, 83.3 mmol) under nitrogen atmosphere was added slowly 1-bromo-4-methylnaphthalene (15 g, 67.8 mmol) in 100 mL of dry ether. The reaction mixture was refluxed for 7–8 h and cooled in an ice bath. Ethylene oxide (3 g, 68.1 mmol) in 10 mL of ether was added slowly, and the reaction mixture was stirred another 0.5 h at room temperature. It was quenched with ice water, extracted with ether, and dried over anhydrous $MgSO_4$. Removal of ether gave 15 g of residue, which was purified over an alumina column to give 10 g of pure **13**; ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.0 (3 H, s), 3.6 (2 H, t), 4.2 (2H, t), 7.5–8.6 (6 H, m).

1-Methyl-4-(2-chloroethyl)naphthalene (13a). To a solution of alcohol **13** (5 g, 26.8 mmol) in 100 mL of dry ether and 2 mL of pyridine was added dropwise 10 mL of thionyl chloride. The resulting solution was refluxed overnight, cooled, and poured over 100 g of ice. Product was extracted with ether, washed with dilute HCl and water, and dried over anhydrous $MgSO_4$. Evaporation of ether gave 5 g of liquid residue, which was passed through silica gel column to get 4.5 g of low-melting solid: mp 31–32 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.95 (3 H, s), 3.5–4.3 (4 H, m), 7.5–8.5 (6 H,m); ^{13}C NMR (ppm, $CDCl_3$) 16.8, 33.76, 41.69, 121.1, 122.4, 122.9, 123.3, 123.6, 124.1, 129.1, 129.4, 130.4, 131.1.

3-Methylbenzo[*a*]spiro[2.5]octa-1,4-dien-3-ol (15). To a solution of ketone **12** (2 g, 11.7 mmol) in 100 mL of dry ether at 0 °C was added dropwise 10 mL of methyllithium (1.6 M in ether) with a syringe needle. The reaction mixture was stirred for 5 h at room temperature. It was then refluxed for 15–20 min, cooled, and quenched with cold water. Product was extracted with ether, dried over anhydrous $MgSO_4$ and evaporated. It gave a white solid residue (1.8 g); mp 116.7 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.4–1.8 (4 H, br d), 1.9 (3 H, s), 3.1 (1 H, s), 5.6

Table II. Carbon-13 NMR Parameters of Different Naphthalenium Ions[a]

ions	carbon-13 chemical shifts and multiplicities												
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_α
 6	181.2 (d)	135.5 (d)	197.3 (s)	133.8 (s)	155.9 (s)	44.2 (t)	133.8 (d)	131.4 (d)	143.1 (d)	130.6 (d)	39.6 (t)	43.1 (t)		
 10	202.2 (s)	129.3 (d)	174.9 (d)	129.8 (s)	151.6 (s)	44.5 (t)	135.7 (d)	127.9 (d)	139.7 (d)	126.4 (d)	38.1 (t)	39.3 (t)		
 2	178.1 (s)	132.3 (d)	180.4 (d)	52.6 (s)	121.6 (d)	137.4 (d)	128.2 (d)	130.3 (d)	132.9 (s)	151.9 (s)	48.5 (t)	48.5 (t)	22.6 (q)	
 14	136.4 (s)	150.1 (d)	129.7 (d)	184.3 (s)	133.1 (d)	130.8 (d)	138.4 (d)	132.2 (s)	136.8 (d)	133.1 (s)	21.8 (q)	23.8 (q)	-	192.7 (d)
 18	175.5 (s)	133.5 (d)	179.7 (d)	53.7 (s)	122.5 (d)	137.9 (d)	129.9 (d)	131.3 (d)	134.6 (s)	154.4 (s)	50.7 (t)	50.7 (t)		
 21	182.8 (s)	128.7 (d)	178.8 (d)	40.5 (s)	119.3 (d)	138.2 (d)	122.1 (d)	128.1 (d)	124.9 (s)	153.0 (s)	37.5 (t)	37.5 (t)		
 22	181.6 (s)	128.1 (d)	178.9 (d)	40.5 (s)	119.0 (d)	137.5 (d)	121.8 (d)	127.3 (d)	124.1 (s)	152.3 (s)	37.9 (t)	37.9 (t)	70.2 (q)	

[a] The phenyl ring carbon resonance of ion 18 were found at $\delta_{^{13}C}$, 137.3, 133.4, 131.9, and 129.9 for different carbon atoms. s = singlet, d = doublet, t = triplet, q = quartet.

(1 H, d), 6.25 (1 H, d), 7.1 (1 H, m), 7.65 (2 H, m), 8.15 (1 H, m).

1-Methyl-4-(1-hydroxyethyl)naphthalene (16). To the Grignard reagent formed from magnesium metal (2 g, 83.3 mmol) and 1-bromo-4-methylnaphthalene (10 g, 45.2 mmol) in 150 mL of dry THF was added dropwise acetaldehyde (2 g, 44.4 mmol) in 10 mL of dry THF at 0 °C, and the reaction mixture was refluxed for 0.5 h. It was quenched with cold water, extracted with ether, washed with bicarbonate and water, and dried over $MgSO_4$. Removal of ether gave 9 g of white solid, which was purified over a silica gel column to get 4 g of pure alcohol: mp 78.6 °C; ^{13}C NMR (ppm, $CDCl_3$) 19.35, 24.2, 66.46, 121.5, 123.5, 124.6, 125.1, 125.32, 126.1, 130.15, 132.57, 133.37, 139.46.

3-Phenylbenzo[a]spiro[2.5]octa-1,4-dien-3-ol (17). To a solution of ketone **12** (3 g, 17.6 mmol) in 30 mL of dry ether at 0 °C was added dropwise 13 mL of phenyllithium (1.9 M solution) with a syringe needle. The solution was stirred at room temperature for 4 h and the reaction was quenched with cold water. Extraction with ether, drying over $MgSO_4$, and evaporation of solvent gave 4.5 g of white solid: mp 80.2 °C; ^{13}C NMR (ppm, $CDCl_3$) 20.19, 20.27, 20.94, 72.7, 120.3, 125.6, 125.8, 126.3, 127.0, 127.4, 127.8, 128.9, 130.1, 132.5, 137.7, 147.9.

1-Phenyl-4-(2-chloroethyl)naphthalene (20). Thionyl chloride (3 mL) in 5 mL of dry ether was added dropwise to a solution of alcohol **17** (2 g, 8.06 mml) and few drops of pyridine in 30 mL of ether. The reaction mixture was refluxed overnight, cooled, and quenched with ice water. Extraction with ether, washing with water, and evaporation of solvent gave 1.5 g of a viscous liquid; ^1H NMR (60 MHz, $CDCl_3$) δ 3.3–3.9 (4 H, m), 7.2–7.7 (9 H, m), 8.0 (2 H, m).

Preparation of CH_3F/SbF_5 Reagent for Methylation. Methyl fluoride was slowly introduced to nearly 0.5 mL of SbF_5 in 1 mL of SO_2 at −80 °C till a clear solution was obtained. There was always an excess of CH_3F present; it was checked by carbon-13 NMR before using the reagent for methylation.

General Procedure for Preparing Ions. All the ions were prepared in a usual manner in the NMR tubes by adding 200–250 mg of neat or SO_2ClF slurry of the substance to a well-stirred solution of 0.5 mL of acid in 2 mL of SO_2ClF or SO_2 at −80 °C or lower temperature.

Acknowledgment. Support of our work by the National Institute of Health is gratefully acknowledged. We would also like to thank Dr. G. Liang for his preliminary investigations and Dr. K. Lammertsma for helpful discussions.

Registry No. 2, 82639-09-6; **5**, 41332-02-9; **6**, 82639-10-9; **8**, 25421-12-9; **9**, 20849-71-2; **10**, 82639-11-0; **12**, 33498-24-7; **12a**, 82639-03-0; **13**, 82639-04-1; **13a**, 58149-75-0; **14**, 82639-05-2; **15**, 82639-06-3; **16**, 58149-67-0; **17**, 82639-07-4; **18**, 82639-12-1; **20**, 82639-08-5; **21**, 82639-13-2; **22**, 82648-55-3.