Nuclear Magnetic Resonance Studies of Some 1-Methyl-, 1-Phenyl-, and 1-Cyclopropyl-1-(2-naphthyl)ethyl Carbonium Ions

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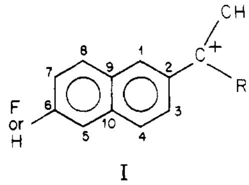
Received October 16, 1978

A series of 1-(2-naphthyl)-1-R-ethyl cations (R = CH_3, C_6H_5, and c-C_3H_5) have been generated from the corresponding alcohols in FSO_3H-SO_2 at low temperatures and their ^{13}C and ^1H spectra were recorded at −70 °C. The spectra have been assigned using well-established criteria and comparisons with the 1-(6-fluoro-2-naphthyl)-1-R-ethyl cation series. In the latter series, ^{19}F chemical shifts have also been measured. When the appropriate remote nucleus, be it ^{13}C, ^{19}F, or ^1H, is monitored as a function of R above, it is clear that when R = c-C_3H_5, least demand for 2-naphthyl resonance is manifested. Interesting trends in $^{13}C-^{19}F$ couplings as R is changed are also observed, and some conclusions regarding preferred conformations in the ions are presented.

There has been considerable discussion in recent years of the relative charge-delocalizing abilities of the methyl, phenyl, and cyclopropyl groups in tertiary ions of the type $(C_6H_5)(CH_3)(R)C^+$. Olah and co-workers[1] have reported extensive ^1H and ^{13}C NMR data for ions of this type and also for similarly substituted allylic cations.[2] Olah's initial conclusion,[3] based largely on the ^{13}C shift of the carbenium center, was that phenyl was more effective than cyclopropyl in charge dispersal. More recently, this view has been somewhat modified in the case of secondary ions for which the sequence c-$C_3H_5 \gtrsim C_6H_5 \gg CH_3$ was arrived at.[2] In addition, Olah[1] recognized that "local influences" can seriously affect the ^{13}C shift of the carbenium ion centers (as the substitution pattern is altered) and such influences are superimposed on bona fide charge (e density) perturbations at this center.[4] On the other hand, solvolytic[5] and equilibrium[7] measurements appear to yield a consistent conclusion; viz. that cyclopropyl is more effective than phenyl in electron release to the ion center. A criticism of the use of solvolytic rate constants to gauge carbonium ion stabilities has been based on the uncertain relationship between the energy of formation of the fully formed ion and that of the ionic transition state from the precursor.[8] This criticism now seems invalid in the light of Arnett's and Petro's[9] recent important measurements, which provide a strong basis for comparison of carbonium ion stabilities through solvolytic rate constants.

The apparent indefiniteness of the ^{13}C approach in yielding reliable orders of carbonium ion stabilizations was in our view very disappointing, as much data now strongly suggests that provided comparable systems are involved and "local influences" on chemical shifts are not a complication, then ^{13}C chemical shifts do provide an extremely useful measure of e-density fluctuations, particularly at conjugated positions in aromatic systems.[10-12] On assessing the situation, we decided that the apparent inconsistency between the ^{13}C and solvolytic data for tertiary ions $(C_6H_5)(CH_3)C^+(R)$ was not due to any fundamental breakdown between the ^{13}C shift/charge density correlations, but that simply the "wrong" ^{13}C shift was being monitored, i.e., the carbenium carbon (C^+) was not a good choice because of the inevitable incursion of "local" or "special influences"[4] when the substitution pattern was altered. Monitoring of the chemical shift of a remote carbon center known to respond sensitively to bone fide e-density changes at C^+ is required to properly assess the value of ^{13}C shifts in relation to charge dispersal by substituents. Our work with the naphthyl ring system[13] had allowed us to determine the response of ring carbons to a wide variety of 1 and 2 substituents, and it seemed to us that data on the ions of structure I below would be most illuminating, particularly the response of C_6 and C_7 for which accurate dependences on resonance (ρ_R) and polar (ρ_I) properties of the 2 substituent were available.[13] The steric situation at position 2 in naphthalene is no worse than that in the corresponding phenyl system.



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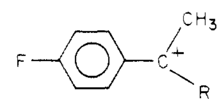

II

R = CH_3, C_6H_5, c-C_3H_5

A study along similar lines using ^{19}F chemical shifts was reported by Volz[14] for system II above, and these shifts were in agreement with solvolytic, equilibrium, and po-

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[1] (a) G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 3548 (1974).

[2] G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.*, **97**, 1539 (1975).

[3] G. A. Olah and P. W. Westerman, *J. Am. Chem. Soc.*, **95**, 7530 (1973).

[4] For general references see: F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra", Heyden, London, 1976; J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.

[5] H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **95**, 2400 (1973); **99**, 1712 (1977).

[6] H. C. Brown, M. Ravindranathan, and E. N. Peters, *J. Org. Chem.*, **42**, 1073 (1977).

[7] N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3051 (1955); N. C. Deno, H. G. Richey, J. S. Liu, D. N. Lincoln and J. O. Turner, *ibid.*, 87, 4533 (1965). See also, H. G. Richey, "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 25.

[8] See for example the discussion in ref 1a.

[9] E. M. Arnett and C. Petro, *J. Am. Chem. Soc.*, **100**, 2563 (1978).

[10] For a summary of evidence and references see: (a) D. A. Forsyth, R. J. Spear, and G. A. Olah, *J. Am. Chem. Soc.*, **98**, 2512 (1976); (b) B. Ancian, F. Membrey, and J. P. Doucet, *J. Org. Chem.*, **43**, 1509 (1978).

[11] M. Bullpitt, W. Kitching, D. Doddrell, and W. Adcock, *J. Org. Chem.*, **41**, 760 (1976).

[12] M. Bullpitt, W. Kitching, W. Adcock, and D. Doddrell, *J. Organomet. Chem.*, **116**, 187 (1976).

[13] W. Kitching, M. Bullpitt, D. Gartshore, W. Adcock, T. C. Khor, D. Doddrell and I. Rae, *J. Org. Chem.*, **42**, 2411 (1977).

[14] H. Volz, J. H. Shin, and H. J. Streicher, *Tetrahedron Lett.*, 1297 (1975).

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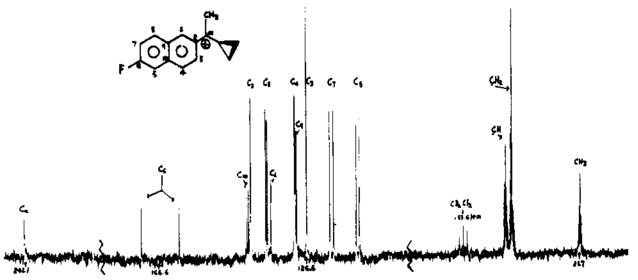

Figure 1. The proton-decoupled 25.2-MHz carbon-13 spectrum (4K accumulations) of 1-(6-fluoro-2-naphthyl)-1-cyclopropylethylcarbonium ion. Solvent is FSO_3H-SO_2 at -70 °C. Chemical shifts are based on the central peak of the CD_2Cl_2 multiplet at +53.6 ppm and are located in Table I along with $^{13}C-^{19}F$ coupling constants.

larographic studies that the cyclopropyl group was a more effective stabilizing group than phenyl.

In this report, we discuss the ^1H, ^{13}C, and ^{19}F studies of the ions I above.

Results

Syntheses. The precursor alcohols were synthesized by standard procedures involving addition of the appropriate Grignard reagent to 2-naphthyl methyl ketone or 6-fluoro-2-naphthyl methyl ketone. The alcohols were characterized by their ^1H, ^{13}C, and ^{19}F spectra and some were contaminated with varying amounts of alkene (elimination), which of course yielded the same cation on protonation. Generation of the ions was achieved by using FSO_3H-SO_2 at -78 °C or lower (alcohols added as CD_2Cl_2 solutions; see Experimental Section) and ionization proceeded smoothly to yield clear rosê to intense red or even purple solutions of the ions. The dimethylnaphthyl ions were least intense in color. Spectra were obtained at ca. -70 °C and the quality of the ^1H and ^{13}C spectra is shown in Figures 1 and 2.

Discussion

^{13}C Spectra. The ^{13}C shifts and $^{13}C-^{19}F$ coupling constants for the six ions examined are located in Table I. Data were available previously for the 1-methyl-1-(2-naphthyl)ethyl cation,[10] and our assignments (and chemical shifts) are in good agreement. Generally, our use of the 6-fluoro derivatives rendered assignments of the spectra of both series (fluoro and nonfluoro) quite straightforward. The basis for this approach[13] has been outlined previously and its utility demonstrated.[15,16] In addition, however, the fluoro derivatives provide very useful information in their own right.

As expected, attachment of $C^+(CH_3)(R)$ to the 2 position of naphthalene induces large substituent chemical shifts at conjugated positions (i.e., C_1, C_{10}, C_6, and C_8) as previously observed[13] for more conventional, neutral election-withdrawing substituents. The magnitude of these effects is shown below in Table II.

Positions 6 and 8 in the 2-naphthyl system, regarded as best able to reflect bona fide changes in resonance interactions,[13] clearly indicate a greater demand for interaction when $R = CH_3 > C_6H_5 > c\text{-}C_3H_5$. This means that *in the conformations accessible by these tertiary ions,* cyclopropyl provides a higher level of electron release to

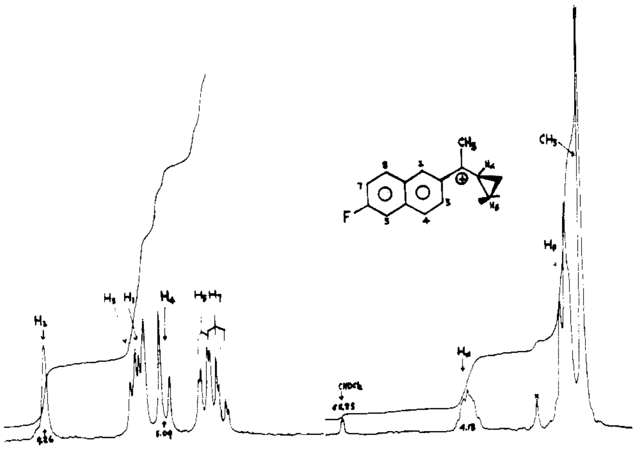

Figure 2. The 100-MHz proton spectrum (100 accumulations) of 1-(6-fluoro-2-naphthyl)-1-cyclopropylethylcarbonium ion. Solvent is FSO_3H-SO_2 at -70 °C, and chemical shifts are based on $CHDCl_2$ at +5.35 ppm. H_7 appears as a triplet of doublets (roughly equal coupling to ^{19}F and H_8 and a smaller coupling to H_5) with the lower field component of the triplet superimposed on the higher field component of the doublet of doublets (coupling to ^{19}F and H_7) due to H_5. H_3 and H_4 approximate to an AB pattern, with H_3 broadened by coupling to H_1. H_8 is a doublet of doublets resulting from coupling to H_7 and ^{19}F, while H_1 is a boradened singlet.

C^+ than does phenyl, and both much greater than methyl. This conclusion is supported by the SCS values at C_{10} as well as C_1, but at the latter position it is conceivable that "local influences" could still operate to some degree.

The trends alluded to above are reproduced faithfully in the data for the corresponding 6-fluoro-2-naphthyl ions (Table I) and the SCS data for these are summarized in Table III, together with the $^{13}C-^{19}F$ couplings, so that variations in these quantities are made clear.

Not unexpectedly,[17] a significant difference in magnitude for the SCS at C_6 is found for the two systems and reflects extended conjugation to fluorine. On the other hand, the SCS values at the conjugated 8 and 10 positions are increased in the 6-F series compared with the 6-H series, consistent with superior conjugation from the fluoronaphthyl system. The negative SCS at C_9 appear to be general for electron-withdrawing 2 substituents.[13] There is an interesting reversal in SCS values at C_3 from positive to negative (for both series, Tables II and III) on progressing from $(CH_3)_2C^+$ and $(CH_3)(C_6H_5)C^+$ to $C^+(CH_3)(c\text{-}C_3H_5)$. We associate this with conformational aspects which will be discussed later.

The variations in $^{13}C-^{19}F$ couplings (Table III) are of interest. As expected,[18] there is a substantial increase in the one-bond $^{13}C-^{19}F$ coupling on progressing from the alcohol ($J \sim 245$ Hz) to the ions, with values of 271.2 ($C^+(CH_3)_2$), 264.62 ($C_+(CH_3)(C_6H_5)$), and 261.3 Hz ($(CH_3)C^+(c\text{-}C_3H_5)$). These trends in J are reproduced at other conjugated positions (e.g., C_8 and C_{10}) and are consistent with least conjugative demands on the 6-F naphthyl system for the $(CH_3)C^+(c\text{-}C_3H_5)$ group, with a lower contribution from the nuclear charge term to the one-bond coupling expression.[18] Couplings at nonconjugated positions, e.g., C_5 and C_7, appear insensitive to changes in R in $C^+(CH_3)R$. An interesting long-range

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[15] W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, and W. Kitching, *J. Org. Chem.*, 41, 751 (1976).

[16] W. Adcock, B. D. Gupta, and W. Kitching, *J. Org. Chem.*, 41, 1498 (1976).

[17] J. Bromilow, R. T. C. Brownlee, R. D. Topsom, and R. W. Taft, *J. Am. Chem. Soc.*, 98, 2020 (1976).

[18] R. J. Spear, D. A. Forsyth, and G. A. Olah, *J. Am. Chem. Soc.*, 98, 2493 (1976).

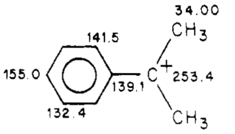
Table I. ^{13}C Chemical Shifts[a] of 1-(2-Naphthyl)-1-substituted-ethyl Cations

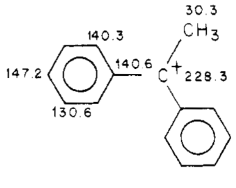
system	ring carbon no. 1	2	3	4	5	6	7	8	9	10	other
I, 6-H											
R = CH_3	152.7	137.2	128.10	131.7	129.4	142.1	130.2	137.2	132.6	144.7	242.4 (C_α), 31.75, 32.40 (CH_3)
	153.2	137.8	128.4	132.1	129.8	142.8	130.8	137.8	133.2	145.5	241.8, 31.8, 31.2[b]
R = c-C_3H_5	142.0	136.8	125.6	130.4	128.6	136.3	129.3	133.9	132.0	140.5	246.8 (C_α), 21.8 (CH_3) 42.5 (CH), 40.8 (CH_2)
R = C_6H_5	143.7	139.0	129.6	131.4	128.9	138.1	130.6	135.0	132.3	141.0	223.1 (C_α), 30.0 (CH_3), 140.9 (C_{ipso}); 139.7 (C_o), 130.6 (C_m) 139.7 (C_p)
I, 6-F											
R = CH_3	151.9	136.8	129.1 (br)	130.8 (4.3)	114.3 (22.1)	170.5 (271.2)	120.9 (25.6)	141.4 (12.5)	130.1	147.6 (13.8)	240.2 (3.4) (C_α), 31.4, 32.1 (CH_3)
R = c-C_3H_5	141.8	136.3 (1.7)	126.6	129.8 (5.0)	112.7 (21.5)	166.6 (261.3)	119.8 (25.7)	137.5 (11.1)	129.3	142.6 (12.0)	241.1 (3.6) (C_α), 21.7 (CH_3), 42.0 (CH), 40.3 (CH_2)
R = C_6H_5	143.5	138.4	130.7	130.8 (~5)	113.4 (21.8)	167.9 (264.6)	120.2 (25.6)	138.9 (11.7)	129.8	143.6 (12.42)	222.1 (br) (C_α), 29.9 (CH_3), 140.9 (C_{ipso}), 139.4 (C_o), 130.7 (C_m), 139.4 (C_p)

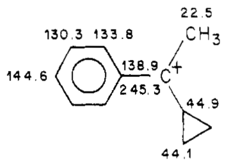
[a] For FSO_3H-SO_2 solutions at ca −70 °C. Chemical shifts based on internal CD_2Cl_2 at 53.6 ppm. [b] Data from ref 10. [c] Values in parentheses are ^{13}C–^{19}F coupling constants.

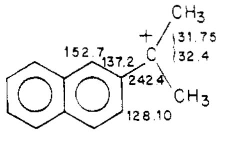
coupling of ca. 3.5 Hz to the carbenium ion carbon is also resolved (Table I).

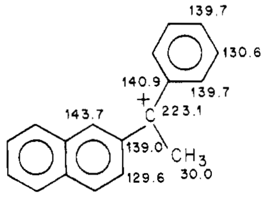
The carbon-13 shifts of the $C^+(CH_3)R$ group have revealing features as well. In the dimethyl cations, the inequivalent methyl signals, previously observed by Olah,[10] are consistent with a relatively high rotational barrier about the C_{aryl}–C^+ bond. This barrier would be expected to be lower as phenyl and cyclopropyl replaced a methyl group. Generally the shifts resemble those reported by Olah for the corresponding phenyl series.

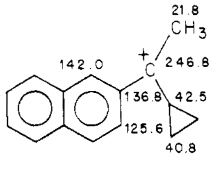




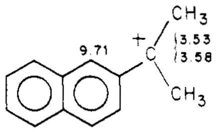


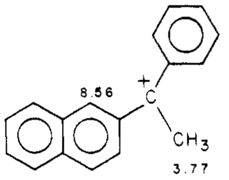


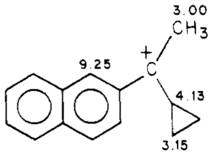


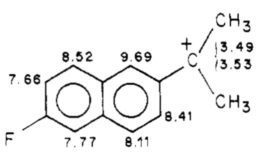


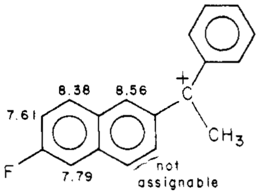
The trends in the C^+ chemical shifts follow the same order for CH_3, C_6H_5, and c-C_3H_5 in both series, but as discussed above, do not provide a valid indication of relative e release from R. An interesting feature concerns the chemical shift of the CH_3 group in the cyclopropyl ions, which are at unusually high-field positions (~22 ppm) compared with the corresponding phenyl and methyl ions (ca. 30–34 ppm). This provides additional insight into the preferred conformations of these ions, as does the shielded nature of C_o (133.8 ppm) in $(C_6H_5)C^+(CH_3)$(c-C_3H_5) and C_3 (125.6 ppm) in the corresponding naphthyl ion.

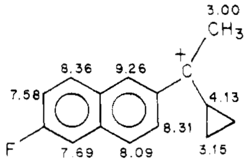












^1H Spectra. The ^1H NMR spectra of the ions generated in this work were also obtained. Assignments of ring proton patterns were generally possible in the cases of the

Table II. Substituent Chemical Shifts[a] (SCS) of 2-$C^+(CH_3)(R)$

	carbon no.									
R =	1	2	3	4	5	6	7	8	9	10
CH_3	+24.0	+10.5	+1.4	+3.0	+.7	+15.4	+3 5	+8.5	-1.8	+10.3
C_6H_5	+15.0	+12.3	+2.9	+2.7	+.2	+11.4	+3.9	+6.3	-2.1	+6.6
c-C_3H_5	+13.3	+10.1	-1.1	+1.7	+.1	+9.6	+2.6	+5.2	-2.4	+6.1

[a] Using chemical shift data[13] for naphthalene in $(CD_3)_2CO$: 128.66 (C_1); 126.67 (C_2); 134.38 (C_9).

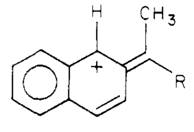
Table III. Substituent Chemical Shifts[a] of 2-$C^+(CH_3)R$ in 6-Fluoro-2-naphthyl Systems

	carbon no.									
R =	1	2	3	4	5	6	7	8	9	10
CH_3	+23.8	+11.6	+2.1	+3.3 (4.3)	+3.4 (22.1)	+9.5 (271.2)	+4.7 (25.6)	10.9 (12.5)	-0.7	+12.9 (13.8)
C_6H_5	+15.4	+13.2	+3.7	+3.3 (~5.0)	+2.5 (21.8)	+6.9 (264.6)	+4.0 (25.6)	8.4 (11.7)	-1.0	+8.9 (12.42)
c-C_3H_5	+13.7	+11.1	-0.4	+2.3 (5.0)	+2.6 (21.5)	+5.6 (261.3)	+3.6 (25.7)	7.0 (11.1)	-1.5	+7.9 (12.0)

[a] Based on reported shifts for 2-fluoronaphthalene.[13]

6-F ions because H_5 and H_7 (flanking fluorine) were significantly shielded, thus increasing the chemical shift range. $^{19}F-^1H$ coupling also proves beneficial for assignment purposes. In the 6-H ions, the ring-proton region is more complex and compressed, and only ^1H, which appears as a lower field broad singlet, could be positively assigned. The chemical shifts are shown, and the multiplicities of the signals were consistent with established trends in $^{19}F-^1H$ and $^1H-^1H$ coupling in aromatic systems.[19] These aspects are made clear in Figure 2.

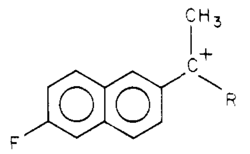
^1H would be anticipated to resonate at quite low field in view of the importance of resonance form i.



i

However, as the steric congestion worsens, e.g., in the R = C_6H_5 ion, the phenyl group cannot be accommodated in a planar way, and must be canted.[20] This now places H_1 increasingly in the shielding zone of the phenyl ring, and renders the H_1 shift an unreliable probe for purely e-density changes. In the 6-F series, the remote H_8 could be assigned and it is clear that the H_8 shift trend is consistent with the sequence of substituent stabilization deduced from the ^{13}C spectra. Another point of interest is the unusual shielding of the CH_3 group (δ 3.00) (which has its counterpart in the ^{13}C spectrum) in the $-C^+(CH_3)(c\text{-}C_3H_5)$ ion. This is indicative of a preferred conformation (see below) about the $C^+(c\text{-}C_3H_5)$ bond. The chemical shifts are otherwise unexceptional.

^{19}F Spectra. The proton-coupled ^{19}F spectra of these ions below were obtained (at -70 °C) and the shifts (ppm relative to internal $CFCl_3$: minus upfield) are shown.

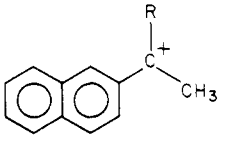


R =	δ	SCS[a]
CH_3	-84.07	+30.68
C_6H_5	-91.26	+23.49
c-C_3H_5	-95.26	+19.49

[a] Based on a chemical shift of -114.75 ppm (with respect to $CFCl_3$ for $CHCl_3$ solvent) for 2-fluoronaphthalene. Positive values to lower field.

The ^{19}F trend is clear and in view of its remoteness from ^+C must be regarded as a reliable monitor of variations in naphthyl resonance in response to changes in R. Clearly, least naphthyl resonance is required when R = c-C_3H_5.

Conformations of the Ions. Rotation about the C^+–naphthyl bond leads to two limiting conformations facilitating naphthyl resonance (A and B). In the case R = c-C_3H_5, variations C and D of B are possible. Similar structures can be drawn for A in which R = c-C_3H_5. Steric congestion between the rear of the cyclopropane ring and H_1 or H_3 would seem to limit the orientation to either C or E (a variation of A). The chemical shifts (^1H or ^{13}C)



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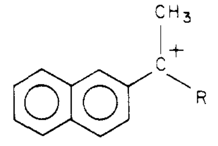
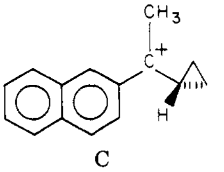


B



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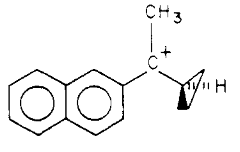

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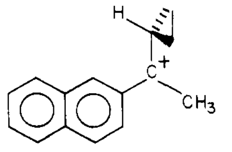

E

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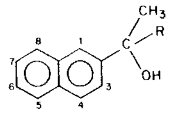
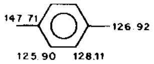
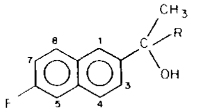
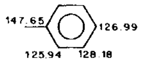
[19] See for example, V. Lucchini and P. R. Wells, *Org. Magn. Reson.*, 8, 137 (1976), and references cited therein.

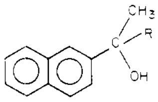
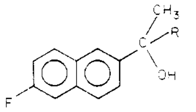
[20] D. G. Farnum, *J. Am. Chem. Soc.*, 86, 934 (1964).

Table IV. Carbon-13 Chemical Shifts[a] of 1-(2-Naphthyl)-1-substituted Ethanols

	carbon no.										
	1	2	3	4	5	6	7	8	9	10	other
											
R = CH_3	122.42	146.48	123.54	127.90	127.46	125.67	126.02	128.13	133.12	132.3	31.63 (CH_3), 72.68 (C-O)
R = c-C_3H_5	123.33	145.54	124.11	127.60	127.43	125.62	125.90	128.18	133.13	132.36	28.47 (CH_3), 1.19 and 2.01 (CH_2), 22.78 (CH), 73.23 (C-O)
R = C_6H_5	123.69	145.24	124.93	127.86	127.42	126.02	126.02	128.20	132.94	132.33	30.58 (CH_3), 76.25 (C-O) 
											
R = CH_3[b]	122.44 (br)	145.84 (2.34)	124.63 (nr)	127.25 (5.41)	110.49 (20.13)	160.59 (245.33)	116.32 (25.48)	130.42 (8.87)	130.17 (nr)	132.94 (9.0)	31.63 (CH_3), 72.52 (C-O)
R = c-C_3H_5[b]	123.41 (br)	145.02 (2.13)	125.26 (nr)	127.01 (5.8)	110.49 (20.15)	160.62 (244.82)	116.23 (25.76)	130.54 (8.88)	130.16 (nr)	133.02 (9.05)	28.45 (CH_3), 73.18 (C-O) 1.20, 2.04 (CH_2), 22.81 (CH)
R = C_6H_5[b,c]	123.70 (br)	144.72 (2.31)	126.03 (nr)	127.21 (6.0)	110.54 (20.08)	160.65 (245.9)	116.25 (25.08)	130.51 (9.65)	129.91 (nr)	132.96 (9.0)	30.47 (CH_3), 76.11 (C-O) 

[a] For $CDCl_3$ solutions referred to internal Me_4Si. [b] Values in parentheses are $^{13}C-^{19}F$ couplings: br = broad; nr = not resolved. [c] Additional signals ascribable to elimination product were observed: 138.17 (2.47) (C_2); 110.64 (20.11) (C_5); 116.39 (25.06) (C_7); 133.58 (9.9) (C_{10}); 149.69 (C=CH_2); 114.81 (C=CH_2); 128 28, 127.84, 141.33 (phenyl ring). Other signals were presumably obscured by the (major) signals of the alcohol.

Table V. $^1H^a$ and $^{19}F^b$ Chemical Shifts of 1-(2-Naphthyl)-1-substituted Ethanols

system	ring position							other	^{19}F shift
	1	3	4	5	6	7	8		
									
R = CH_3	7.90	←		7.38-7.9			→	1.63 (CH_3), 2.16 (OH)	
R = c-C_3H_5	7.94	←		7.36-7.98			→	1.51 (CH_3), 1.95 (OH), 1.26 (CH), 0.43 (CH_2)	
R = C_6H_5	7.92	←		7.1 -7.96			→	1.44 (CH_3), 2.5 (OH) (C_6H_5 in naphthyl region)	
									
R = CH_3	7.89	7.60	7.70	7.39		7.21	7.75	1.63 (CH_3), 2.14 (OH)	−115.67 −115.22^c
R = c-C_3H_5	7.96	7.68	7.68	7.41		7.22	7.80	1.55 (CH_3), 1.82 (OH), 1.31 (CH) 0.5 (CH_2)	−115.68
R = C_6H_5^{d}	7.92	←		7.06-7.96			→	1.97 (CH_3), 2.46 (OH) (C_6H_5 in naphthyl region)	115.27 −114.82^c

[a] Referred to internal Me_4Si for $CDCl_3$ solvent, 100 MHz. [b] Referred to internal $CFCl_3$, 94.1 MHz. Fluorobenzene at −113.41 ppm. [c] Minor ^{19}F signal associated with alkene elimination product. [d] A signal at δ 5.55 associated with $=CH_2$ of alkene.

of CH_3 in the cyclopropyl ions are at unusually high field but consistent with arrangements C or E in which the CH_3 group is located approximately near the threefold axis of the cyclopropyl group.

For the ions in which R = C_6H_5 and c-C_3H_5, the discrete existence of isomeric ions of both A and B types is not observed, despite the distinct CH_3 signals in the dimethyl (i.e., R = CH_3 in A) ions. This could mean that one isomeric ion is substantially favored or that the barrier to rotation about the naphthyl–C^+ bond is sufficiently low. As C_6H_5 and c-C_3H_5 replace CH_3, it is expected that this barrier will be lowered, as a reduced demand for naphthyl resonance will result with a lower naphthyl–C^+ bond order.

When R = C_6H_5 or c-C_3H_5, it is not clear whether conformer A or B should be favored. It would be expected that the "intrinsic" H_1 shift when R = C_6H_5 or c-C_3H_5 would be upfield compared with H_1 when R = CH_3, as a consequence of reduced naphthyl resonance. However the H_1 shifts of δ 8.56 (R = C_6H_5) and δ 9.25 (R = c-C_3H_5) are inappropriate as reflections of purely resonance interactions with the side chain. (A reversed order would be anticipated.) It is reasonable that as the steric congestion worsens, e.g., when R = C_6H_5, the phenyl group cannot be accommodated in a planar way and must be canted.[20] This now places ^1H increasingly in the shielding zone of the phenyl ring, and indicates the presence of a substantial population of A (R = C_6H_5). When R = c-C_3H_5, conformer E might result in some deshielding of H_1, while in C there would be little effect at H_1. Unfortunately H_3 could not be assigned in the phenyl series of ions and thus information on its chemical shift fluctuations with changes in R was not available. However, C_3 in all ions could be assigned, and the ^{13}C SCS at this position are irregular as R is varied, becoming slightly negative when R = c-C_3H_5. This could be associated with conformer C, which places the unique cyclopropyl hydrogen and H_3 in close proximity in the favored "bisected" geometry. However, in conformation E this presumed (shielding) effect at C_1 would be minor in comparison with the very large resonance deshielding, which of course is inoperative in the region of C_3. The above considerations apply to the 6-F series of ions, as the trends in ^1H and ^{13}C shifts are very similar.

Examination of other series of naphthyl–methyl cations are underway and will be reported in the near future.

Experimental Section

Compounds. The alcohols were synthesized by reacting methyl, phenyl, or cyclopropyl Grignard reagents with either 2-naphthyl methyl ketone or 6-fluoro-2-naphthyl methyl ketone[21] in a standard way, followed by a normal workup procedure. All compounds were completely characterized by ^1H, ^{13}C, and where appropriate ^{19}F NMR spectra.

1-(2-Naphthyl)-1-methylethanol: mp 63.5–64 °C (lit. 63–64.5 °C[22] and 66 °C[23]).

1-(6-Fluoro-2-naphthyl)-1-methylethanol: mp 58–59 °C; *m/e* 204.

1-(2-Naphthyl)-1-phenylethanol was obtained as a very viscous oil, contaminated with some alkene, and was characterized by ^1H and ^{13}C NMR.

1-(6-Fluoro-2-naphthyl)-1-phenylethanol was a viscous oil also contaminated with some alkene, *m/e* 266.

1-(2-Naphthyl)-1-cyclopropylethanol was a viscous oil as was **1-(6-fluoro-2-naphthyl)-1-cyclopropylethanol.**

The ^{13}C NMR spectra of the alcohols are located in Table IV and the ^1H and ^{19}F spectra are in Table V.

All compounds provided spectra consistent in detail with the indicated structures.

Preparation of Ions. The ions were prepared in 10-mm NMR tubes adapted for operations such as evacuation and N_2 purging followed by vacuum sealing. The procedure has been fully described by Brookhart.[24] Normally a 3:1 solution of SO_2–FSO_3H (ca. 2 mL) was prepared and cooled to at least −78 °C. A cooled solution of the alcohol (∼75 mg) in CD_2Cl_2 (∼0.2 mL) was added dropwise with a micropipet with vigorous stirring. Highly colored solutions of the ions resulted. The solutions were then frozen (liquid N_2) and sealed under vacuum. The solutions of the 6-fluoro-2-naphthyl ions also contained a small amount of $CFCl_3$ for internal referencing for ^{19}F shift measurement. The CD_2Cl_2 also provided the ^2H lock signal for the XL-100 spectrometer. On some occasions minor signals in the ^{13}C and ^1H spectra indicated alkylation and/or polymerization, etc. Ion preparation in these cases was repeated, and it was found advantageous on occasions to reverse the addition sequence in ion preparation. Thus, the CD_2Cl_2 solution of the alcohol was thoroughly mixed and dispersed in the SO_2 at at least −78 °C. Then the cold FSO_3H was added dropwise with vigorous stirring and clean solutions of the ions were obtained.

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(21) W. Adcock, M. J. S. Dewar, R. Golden, and M. A. Zeb, *J. Am. Chem. Soc.*, **97**, 2198 (1975).

(22) Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **79**, 1903 (1957).

(23) R. H. Pickhand and J. Kenyon, *J. Am. Chem.*, **105**, 115 (1914).

(24) M. Brookhart, E. R. Davis, and D. L. Harris, *J. Am. Chem. Soc.*, **94**, 7853 (1972).

NMR Spectra. The ^1H, ^{13}C, and ^{19}F spectra were recorded for the indicated solvents and conditions on a Varian XL-100 spectrometer. ^1H spectra were referred to internal $CHDCl_2$ (δ 5.35) as secondary standard, while the center of the CD_2Cl_2 multiplet in the ^{13}C spectrum was taken as + 53.6 ppm. ^{19}F spectra were referred to internal $CFCl_3$.

Acknowledgments. Part of this work was conducted while one of us (W.K.) was a Visiting Professor in the Department of Chemistry, University of North Carolina at Chapel Hill. W.K. is indebted to the Department there for generous hospitality, and in particular to Professor Maurice Brookhart for advice and laboratory facilities, and to Dr. David Harris for his expertise with the Varian-XL-100 NMR spectrometer.

Note Added in Proof: Professor Volz (Universität Karlsruhe) has kindly informed us that in ion series II, the one-bond $^{19}F-^{13}C$ couplings decrease from 294.1 Hz (R = CH_3) through 282.38 Hz (R = C_6H_5) to 276.5 Hz (R = c-C_3H_5). This trend is in agreement with that reported herein for ion series II.

Registry No. 2-Naphthyl methyl ketone, 93-08-3; 6-fluoro-2-naphthyl methyl ketone, 33627-02-0; 1-(2-naphthyl)-1-methylethanol, 20351-54-6; 1-(6-fluoro-2-naphthyl)-1-methylethanol, 55831-07-7; 1-(2-naphthyl)-1-phenylethanol, 69726-39-2; 1-(6-fluoro-2-naphthyl)-1-phenylethanol, 69726-40-5; 1-(2-naphthyl)-1-cyclopropylethanol, 69726-41-6; 1-(6-fluoro-2-naphthyl)-1-cyclopropylethanol, 69745-65-9; 1-methyl-1-(2-naphthyl)ethylium, 25401-60-9; 1-cyclopropyl-1-(2-naphthyl)ethylium, 69726-42-7; 1-phenyl-1-(2-naphthyl)ethylium, 69726-43-8; 1-(6-fluoro-2-naphthyl)-1-methylethylium, 69726-44-9; 1-cyclopropyl-1-(6-fluoro-2-naphthyl)ethylium, 69726-45-0; 1-(6-fluoro-2-naphthyl)-1-phenylethylium, 69726-46-1.

Halogen Complexes of Pyridines. A Proton and Carbon-13 Nuclear Magnetic Resonance Study[1a]

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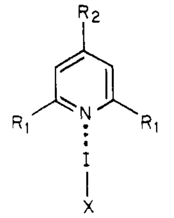
Contribution No. 5969 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125

Received February 12, 1979

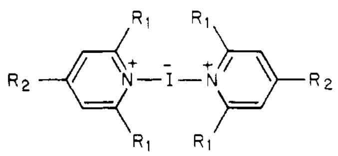
Solutions of iodine and iodine chloride with pyridine, 2,6-dimethylpyridine, and 2,4,6-trimethylpyridine were studied by ^1H and ^{13}C NMR. Support is deduced for the reported formation of three species: the charge-transfer complex B·X–I, the 1:1 complex $^+B-I[X_nI_{n-1}^-]$, and the *N*-iododipyridinium salt $^+B_2I[X_nI_{n-1}^-]$. The ease of formation of each species appears to be a function of pyridine basicity, the Lewis acidity of the halogen (I_2 or ICl), the solvent polarity, and the relative donor–acceptor concentrations. The complexes derived from α-methyl-substituted pyridines can be distinguished by the magnitudes and directions of their ^{13}C "iodination" shifts.

Studies of complexes between IX (X = Cl, Br, I, CN) and pyridines have involved spectroscopic methods, measurements of the electrical conductivities of their solutions, and X-ray analyses of the more stable forms in the solid state.[2] There is ample evidence that charge-transfer complexes, 1, are formed in dilute solutions when solvents of low dielectric constant are used. In polar media, the formation of an ionic species is favored, the cation[3] of which has been variously assigned structures 2 and 3 by different groups of workers.[4-8] The crystal structures of solids corresponding to 1 and 2 have been determined for some IX complexes of pyridines. Formation of both 1 and 2 in solution has been postulated by Larsen and Allred[9]



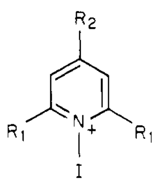
$(I_{n-1}X_n)^-$

1



$(I_{n-1}X_n)^-$

2



$(I_{n-1}X_n)^-$

3

$R_1 = R_2 = H$ or CH_3

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[1] (a) Supported by the National Science Foundation and by the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences. (b) On sabbatical leave from Pennsylvania State University, Ogontz Campus, 1977–1978.

[2] For reviews see: Andrews, L. J.; Keefer, R. M. *Adv. Inorg. Chem. Radiochem.* **1961**, *3*, 91–133. Briegleb, G. "Elektronen-Donator-Acceptor-Komplexe"; Springer Verlag: Berlin, 1961. Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969.

[3] The nature of the anions 2 and 3 appears to be solvent and concentration dependent. For 2 (X = I), species ranging from I_3^- to I_9^- have been proposed.

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