

Stable Carbocations. 254.¹ Direct Preparation of 9- α -Ethyleneanthracenium Ions from 9- β -Fluoroethylanthracenes via Anthryl Participation and Their ¹H and ¹³C NMR Spectroscopic Study

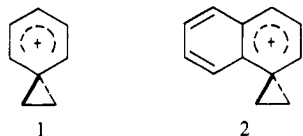
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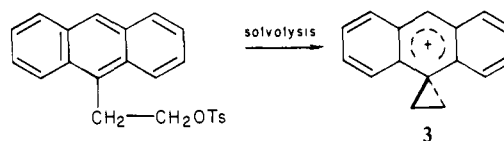
Abstract: Ebersson and Winstein in 1965 were able to prepare the 9- α -ethyleneanthracenium ion (3) from 9-spirocyclopropyl-10-hydroxy-9,10-dihydroanthracene (10) with SbF₅-SO₂ClF solution. Attempts to prepare this ion from 9- β -haloethylanthracenes via aryl participation were unsuccessful, and only σ complexes with SbF₅ were observed. Whereas ethylenebenzenium ("phenonium") and naphthalenium ions were obtained in our preceding work from the corresponding β -haloethyl precursors via aryl participation, similar preparation of 9- α -ethyleneanthracenium ions remained elusive. Attempted ionization of 9-(β -chloroethyl)anthracene (4) and 9-(β -chloroethyl)-10-methylanthracene (12) in FSO₃H-SO₂ClF at -78 °C gave instead the corresponding anthracenium ions (i.e., ring-protonated anthracenes) 5 and 13. Similarly, 9-(β -fluoroethyl)anthracene (7) and 9-(β -fluoroethyl)-10-methylanthracene (14) in FSO₃H-SO₂ClF or HF-BF₃/SO₂ClF at -90 °C gave the corresponding anthracenium ions 8 and 15a,b, without any ionization of the β -fluoroethyl group. Ionization of precursors 7 and 14 with SbF₅ in SO₂ClF solution at -90 °C, however, gave the so far elusive 9- α -ethyleneanthracenium ion (3) and 9-(α -ethylene)-10-methylanthracenium ion (16), respectively, by direct anthryl participation and were observed by ¹H and ¹³C NMR spectroscopy. Ions 3 and 16 were also prepared independently from other precursors such as 10 and 12a. Ionization of phenyl-substituted spirocyclic tertiary alcohol 19 gave the phenyl-substituted 9- α -ethyleneanthracenium ion (20).

Participation by aryl groups in the solvolysis of 2-arylethyl derivatives was first proposed by Cram² and studied extensively.³ The involvement of σ -bridged ethylenebenzenium ion (1) and ethylenenaphthalenium ion (2) was a question of controversy⁴ but

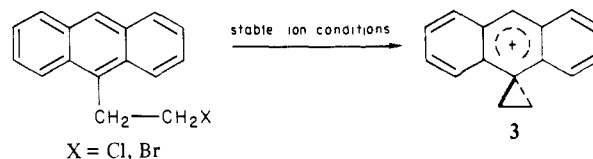


is now well established helped by direct observation of long-lived ions under stable ion conditions.^{5,6} Similar participation by an anthryl group has been proposed by Winstein et al. in the solvolysis and deuterium-scrambling studies⁷ involving 9- α -ethyleneanthracenium ion (3) as an intermediate. Ebersson and Winstein were able to prepare and study 3 by ¹H NMR spectroscopy under stable ion⁸ conditions, however, only from 9-spirocyclopropyl-10-hydroxy-9,10-dihydroanthracene, an alcohol having preformed spirocyclopropane ring present in the molecule. Consequently, that does not prove the direct participation of anthryl group.

To observe direct anthryl group participation in the ionization of 9- β -ethylantracene derivatives under stable ion conditions



remained a challenge. In continuation of our studies of ethylenebenzenium and naphthalenium ions we now wish to report our success to achieve this goal in directly preparing the elusive 9- α -ethyleneanthracenium ion 3 and its substituted homologues and report their study by proton and carbon-13 NMR spectroscopy.



Results and Discussion

Preparation and Observation of 9- α -Ethyleneanthracenium Ion (3). When 9-(β -chloroethyl)anthracene (4)^{9,10} was added to a solution of FSO₃H-SbF₅, SbF₅, or HF:SbF₅ in SO₂ClF at -80 °C ion 3 was not obtained. The resulting solution immediately turned dark brown and only unidentifiable broad NMR signals were observed in all probability due to the oxidation of the anthracene ring system by SbF₅ to give radical cations. Ionization of 4 in FSO₃H/SO₂ClF at -78 °C resulted in exclusive ring protonation giving anthracenium ion 5 without any ionization of the β -chloroethyl group. The ¹³C NMR of ion 5 showed ten signals as shown in Table II. The peaks in the aliphatic region at $\delta_{(13C)}$ 38.1, 33.2, and 44.8 are assigned to C-10, C-15, and C-16, respectively. The most deshielded peak at $\delta_{(13C)}$ 195.5 is assigned to C-9. Another low-field peak at $\delta_{(13C)}$ 153.3 is assigned to C-12, C-13. The ¹³C NMR chemical shifts of ion 5 are comparable to those for reported protonated 9-methylanthracene (6).¹¹

(9) Chlorides 4 and 12 were prepared from the corresponding alcohols 4a and 12c with use of SOCl₂/pyridine reagent; see Experimental Section.

(10) Alcohol 4a was prepared by the procedure reported by Mikhailov: Mikhailov, B. M. *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk (Bull. Acad. Sci. URSS, Classe Sci. Chim.)*, (1948), 420-6; *Chem. Abstr.* 1948, 43, 2081.

(1) Stable Carbocations. 254. For part 253, see: Krishnamurthy, V. V.; Prakash, G. K. S.; Iyer, P. S.; Olah, G. A. *J. Am. Chem. Soc.*, submitted.

(2) Cram, D. J. *J. Am. Chem. Soc.* 1949, 71, 3863; 1952, 74, 2129; 1964, 86, 3767.

(3) For a review, see: Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. "Carbenium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. 3, pp 1347-1483 and references therein.

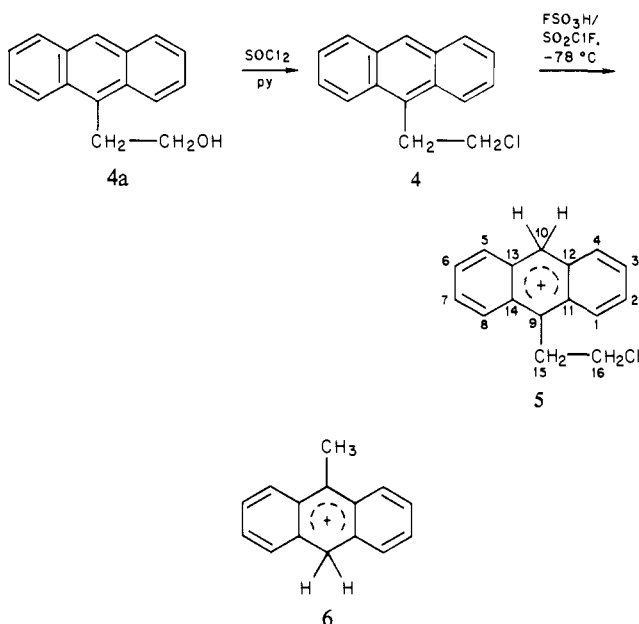
(4) Brown, H. C.; Morgan, K. J.; Chloupek, F. J. *J. Am. Chem. Soc.* 1965, 87, 2137.

(5) (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. "Carbenium 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, 7672. (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.

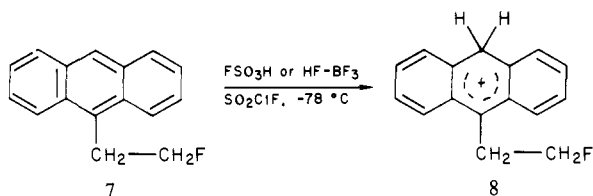
(6) Olah, G. A.; Singh, B. P. *J. Am. Chem. Soc.* 1982, 104, 5168.

(7) Ebersson, L.; Petrovich, J. P.; Baird, R.; Dyckes, D.; Winstein, S. *J. Am. Chem. Soc.* 1965, 87, 3504.

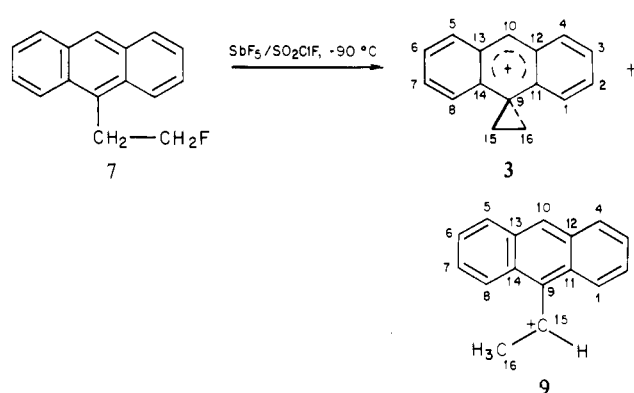
(8) Ebersson, L.; Winstein, S. *J. Am. Chem. Soc.* 1965, 87, 3506.



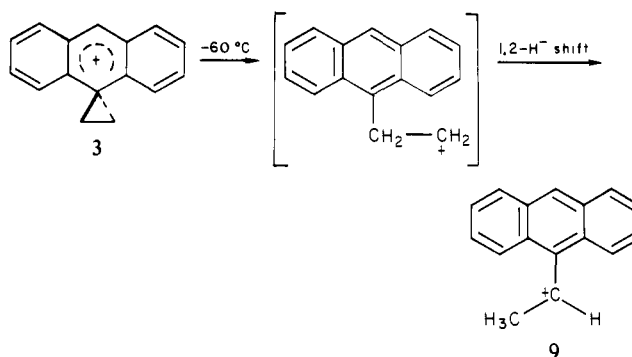
As alkyl fluorides are ionized with Lewis acid halides more readily than alkyl chlorides or bromides we prepared 9-(β -fluoroethyl)anthracene (**7**)¹² from 9-(β -hydroxyethyl)anthracene (**4a**)¹⁰ (see Experimental Section). Ionization of **7** in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ or $\text{HF}-\text{BF}_3$, a nonoxidizing medium, at -78°C gave only protonation of the aromatic ring, i.e., ion **8**, again without any ionization at the β -fluoroethyl group. The structure of ion **8** was proved by its ^{13}C NMR spectrum (Table II). The lowest field peak at $\delta_{(^{13}\text{C})}$ 197.4 is assigned to C-9. The signals at $\delta_{(^{13}\text{C})}$ 33.4 (a doublet, $J_{\text{C-F}} = 19.7$ Hz) and 84.5 (a doublet, $J_{\text{C-F}} = 175.1$ Hz) are assigned to C-15 and C-16, respectively. The C-10 methylene is at $\delta_{(^{13}\text{C})}$ 38.8. The assignment of the additional carbon peaks are as shown in Table II and are again comparable with those of protonated 9-methylantracene (**6**).¹¹ Slow addition of **7** to a solution of SbF_5 in SO_2ClF at -90°C , however, gave a



redish brown solution whose ^1H and ^{13}C NMR spectra showed it to be the elusive 9- α -ethyleneanthracenium ion (**3**) with a trace amount of benzylic ion **9** also present (Figure 1a). The 200-MHz ^1H spectrum of ion **3** shows six sets of peaks which are assigned as in Table I. In this ion C-10 can be considered as a para-like position with respect to the spiro carbon C-9. Hence the most deshielded resonance at δ 10.5 is assigned to H_{10} . Since the ortho-like positions C-11 and C-14 do not contain any protons, the other two low-field resonances at δ 8.4 and 7.9 are assigned to H_4 , H_5 and H_2 , H_7 , respectively, deshielded by delocalized positive charge through related resonance structures. The symmetrical cyclopropane methylene protons H_{15} , H_{16} are assigned at δ 2.6. The ^{13}C NMR spectrum of ion **3** is shown in Figure 1a, with assignments¹³ given in Table II. The most deshielded signal at $\delta_{(^{13}\text{C})}$ 172.6 is that of C-10. The proton coupled ^{13}C spectrum of ion **3** enabled assignments of C-11, C-14 and C-12, C-13 at $\delta_{(^{13}\text{C})}$ 160.0 and 131.9, as well as of the spiro carbon C-9



and symmetrical cyclopropane methylenes C-15, C-16 at $\delta_{(^{13}\text{C})}$ 40.7 and 45.9, respectively. The other deshielded ring carbons C-2, C-7 and C-4, C-5 (affected by delocalized positive charge) are assigned at $\delta_{(^{13}\text{C})}$ 143.8 and 139.0. These assignments, however, may be interchangeable. The remaining four ring carbons C-3, C-6 and C-1, C-8 are at $\delta_{(^{13}\text{C})}$ 129.6 and 123.0. Presence of a singlet at δ 2.6 in the ^1H spectrum and two signals in the ^{13}C NMR at $\delta_{(^{13}\text{C})}$ 40.7 (C-9, spiro carbon) and $\delta_{(^{13}\text{C})}$ 45.8 (C-15, C-16, symmetrical methylenes) together with other features of ^1H and ^{13}C spectra clearly prove it to be the 9- α -ethyleneanthracenium ion (**3**). Upon allowing the temperature of the above solution containing ion **3** and traces of ion **9** to rise to -60°C , ion **3** disappeared and the brown solution is that of only ion **9**. This is in accord with the ready opening of the cyclopropane ring to a primary β -anthrylethyl cation which then immediately rearranges via 1,2-hydrogen shift to more stable secondary benzylic ion **9**.



The presence of observed traces of ion **9** in the -90°C spectrum of ion **3** may also be explained in the same way due to local overheating during preparation of ion from precursor **7**. The ^{13}C spectrum (Figure 1b) shows 16 signals which indicates that ion **9** is unsymmetrical. In fact, this is expected in the frozen out form of ion **9**. The most deshielded signal at $\delta_{(^{13}\text{C})}$ 170.0 is assigned to C-15, a benzylic carbocationic center bearing substantial positive charge. The proton-coupled spectrum of ion **9** enabled assignments of C-10, C-11, and C-14 at $\delta_{(^{13}\text{C})}$ 166.4, 145.9, and 140.6. The difference between the chemical shifts of C-11 and C-14 may be explained on the basis of "substituent effect",¹⁴ where the carbon center "syn" to C-16 methyl is shielded compared to one which is "anti". Similarly, C-12 and C-13 are assigned at $\delta_{(^{13}\text{C})}$ 132.1, 131.4. The remaining eight peaks in the spectrum are assigned as shown in Table II. The structure of ion **3** was further proved by comparing it with the independently prepared ion following Ebersson and Weinstein's procedure, i.e., from precursor spirocyclopropyl alcohol **10**. Precursor **10** was prepared by a series of reactions as shown in Scheme I. Ionization of alcohol **10** in $\text{SbF}_5/\text{SO}_2\text{ClF}$ at -80°C gave a redish brown solution. The ^{13}C spectrum (Figure 1c) and ^1H NMR of the above solution were found exactly superimposable to those of ion **3** formed from precursor **7**.

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

(12) Compounds **7** and **14** were prepared from the corresponding alcohols **4a** and **12c** by the method reported by Middleton: Middleton, W. J. *J. Org. Chem.* **1975**, *40*, 574.

(13) Assignments of ^1H and ^{13}C NMR of all 9- α -ethyleneanthracenium ions **3**, **16**, and **20** were made on the basis of (a) resonance multiplicities in proton coupled spectrum, (b) resonance relative intensities, and (c) comparison of ^{13}C spectrum to protonated anthracenes.¹¹

(14) Olah, G. A.; Westerman, P. W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 3419 and references cited therein.

Table I. Proton NMR Parameters of Anthracenium Ions

ions	proton chemical shifts ^a and multiplicities ^b											others
	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	H ₈	H ₁₀	H ₁₅	H ₁₆	
3	7.3 (d)	7.9 (t)	7.6 (t)	8.4 (d)	8.4 (d)	7.6 (t)	7.9 (t)	7.3 (d)	10.5 (d)	2.6 (s)	2.6 (s)	
16	7.1 (d)	7.7 (t)	7.3 (t)	8.2 (d)	8.2 (d)	7.3 (t)	7.7 (t)	7.1 (d)		2.8 (s)	2.8 (s)	CH ₃ , 3.0 (s)
20	7.0 (d)	7.7 (t)	7.2 (t)	7.5 (d)	7.5 (d)	7.2 (t)	7.7 (t)	7.0 (d)		3.0 (s)	3.0 (s)	phenyl, 7.2 (br s)
9	7.8 (d)	7.9 (t)	7.4 (t)	8.0 (d)	8.0 (d)	7.5 (t)	7.9 (t)	7.8 (d)	9.1 (s)	8.4 (q)	2.3 (d)	
17	7.8 (d)	7.7 (t)	7.4 (t)	8.1 (d)	8.2 (d)	7.4 (t)	7.7 (t)	7.9 (d)		8.0 (q)	2.2 (d)	CH ₃ , 3.0 (s)

^a Chemical shifts are in parts per million from external Me₄Si. ^b Multiplicities are in parentheses: s = singlet, d = doublet, t = triplet, q = quartet, br = broad.

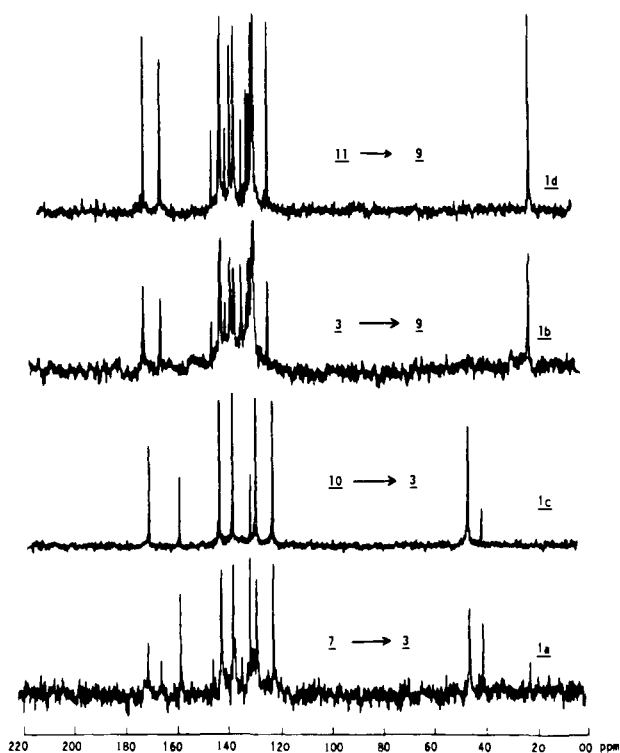
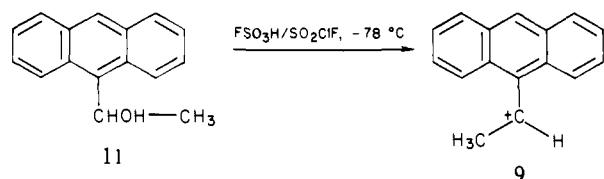


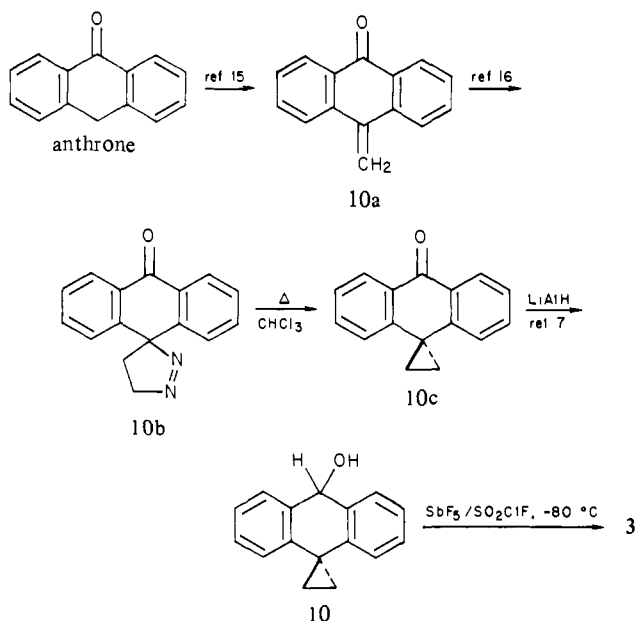
Figure 1. Carbon-13 spectra of ions 3 and 9.

Similarly, structure of ion 9 was further proved by preparing it independently from benzylic alcohol **11**.¹⁷ Ionization of **11** in FSO₃H/SO₂ClF at -78 °C gave a clear yellowish red solution. The ¹³C spectrum (Figure 1d) of this solution is identical with that obtained from precursor **7** at -60 °C (see Figure 1b, 1d). The ¹H NMR parameters of ion 9 and their assignment are given in Table I. The resonance at δ 2.3 is assigned to H₁₆. H₁₀ and H₁₅ are assigned at δ 9.1 and 8.4 on the basis of their multiplicities. The other assignments are, however, not unequivocally established and may be interchanged.



Preparation of 9-(α -Ethylene)-10-Methylanthracenium Ion (16). The preparation of this ion was carried out from 9-(β -chloro-

Scheme I



ethyl)-10-methylanthracene (**12**)⁹ which was prepared from the corresponding 9-(β -hydroxyethyl)-10-methylanthracene (**12c**).¹⁸ Alcohol **12c** was prepared through a series of reactions as given in Scheme II. Ionization of 9-(β -chloroethyl)-10-methylanthracene (**12**) in SbF₅, FSO₃-SbF₅, or HF-SbF₅ at -78 °C or lower temperature gave a dark brown solution, ¹³C spectrum of which showed very broad signals. This may again be due to oxidation of the aromatic ring by SbF₅ to give radical cation. Addition of **12** to a solution of FSO₃H/SO₂ClF or HF:BF₃/SO₂ClF at -90 °C on the other hand resulted in the protonation of the aromatic ring to give ion **13**. The ¹³C spectrum of this ion shows eleven resonances. The most deshielded signal at $\delta_{(^{13}\text{C})}$ 200.8 is that of C-10. The next lower field signal at $\delta_{(^{13}\text{C})}$ 154.9 is assigned to C-11, C-14. The proton-coupled spectrum enabled assignments for C-12, C-13 at $\delta_{(^{13}\text{C})}$ 132.8 and for C-9, C-15, C-16, and C-17 at $\delta_{(^{13}\text{C})}$ 44.2, 40.2, 43.8, and 20.6, respectively. The assignments of the additional four peaks are as shown in Table II. The chemical shifts of ion **13** are again comparable to those reported for protonated 9-methylanthracene (**6**).¹¹ One could also argue about the possibility of protonation at the C-10 position (i.e., para to the β -chloroethyl chain at C-9) of **12** but the presence of eleven resonances in the ¹³C spectrum as well as the observed 6.4-ppm deshielding in the chemical shift of the methyl group at C-10 clearly shows that protonation occurred exclusively at C-9 giving a single ion **13**. In contrast 9-(β -fluoroethyl)-10-methylanthracene (**14**)¹² in FSO₃H/SO₂ClF at -80 °C gives protonation at C-9 to form ion **15a** while in the nonoxidizing superacid HF-BF₃ at -90 °C gave protonation at both C-9 and C-10 carbons giving rise to a mixture of two ions **15a** and **15b**. The ¹³C spectrum indicates formation of both ions **15a** and **15b**, with assignments tentatively as in Table II. The replacement of a chlorine by a fluorine in

(15) Starnes, W. H., Jr. *J. Org. Chem.* **1970**, *35*, 1974.
 (16) Mustafa, A.; Hilmy, M. K. *J. Chem. Soc.* **1952**, 1434. A high yield of **10c** was easily obtained by using less than 2 equiv of diazomethane solution (see Experimental Section), as compared to the negative results reported by Rosenfield²⁰ using a tenfold excess of CH₂N₂. We were also able to isolate the intermediate compound **10b** which was confirmed by its ¹H and ¹³C NMR data. ¹H NMR (CDCl₃) δ 2.5 (t, 2 H), 5.4 (t, 2 H), 7.1 (m, 2 H), 7.9 (t, 4 H), 8.7 (m, 2 H). ¹³C NMR (CDCl₃) $\delta_{^{13}\text{C}}$ 27.7, 36.6, 80.3, 126.4, 127.9, 129.0, 130.7, 134.4, 142.2, 184.0.

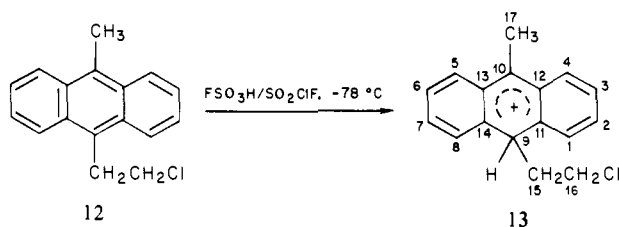
(17) Alcohol **11** was prepared by the procedure of Fieser and Hartwell: Fieser, L. F.; Hartwell, J. L. *J. Am. Chem. Soc.* **1938**, *60*, 2555.

(18) Alcohol **12c** was prepared by lithium aluminum hydride reduction of acetate **12b** (see Experimental Section).

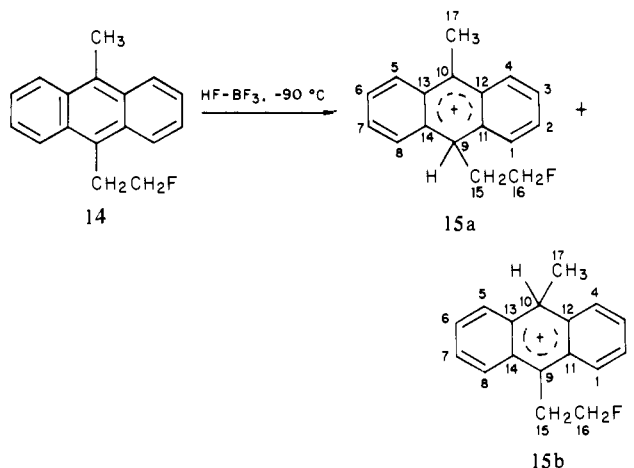
Table II. Carbon-13 NMR Parameters of Anthracenium Ions

ions	carbon-13 chemical shifts ^a and multiplicities ^b																	
	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 ₁₄	C ₁₅	C ₁₆	C ₁₇	
5	134.8 (d)	129.9 (d)	143.8 (d)	129.6 (d)	129.6 (d)	143.8 (d)	129.9 (d)	134.8 (d)	195.5 (s)	38.1 (t)	132.1 (s)	153.3 (s)	153.3 (s)	132.1 (s)	33.2 (t)	44.8 (t)		
8	135.7 (d)	130.4 (d)	144.6 (d)	130.4 (d)	130.4 (d)	144.6 (d)	130.4 (d)	135.7 (d)	197.4 (s)	38.8 (d)	133.2 (s)	154.0 (s)	154.0 (s)	133.2 (s)	33.4 [C ₉ -F = 175.1]	84.5 [C ₉ -F = 175.1]		
3	123.0 (d)	143.8* (d)	129.6 (d)	139.0* (d)	139.0* (d)	129.6 (d)	143.8* (d)	123.0 (d)	40.7 (s)	172.6 (d)	160.0 (s)	131.9 (s)	131.9 (s)	160.0 (s)	45.9 (t)	45.9 (t)		
9	129.4 (d)	142.8 (d)	129.8 (d)	138.7 (d)	137.2 (d)	130.3 (d)	142.4 (d)	124.0 (d)	134.3 (s)	166.4 (d)	145.9 (s)	132.1 (s)	131.4 (s)	140.6 (s)	173.0 (d)	21.1 (q)		
13	129.8 (d)	144.2 (d)	129.8 (d)	136.2 (d)	136.2 (d)	129.8 (d)	144.2 (d)	129.8 (d)	44.2 (d)	200.8 (s)	154.9 (s)	132.8 (s)	132.8 (s)	154.9 (s)	40.2 (t)	43.8 (t)		
15a ^c	130.8 (d)	145.1 (d)	130.8 (d)	137.0 (d)	137.0 (d)	130.8 (d)	145.1 (d)	130.8 (d)	44.6 (d)	201.8 (s)	156.3 (s)	133.5 (s)	133.5 (s)	156.3 (s)	42.5 (t)	80.7 (t)		20.6 (q)
15b ^c	136.7 (d)	130.6 (d)	144.8 (d)	130.6 (d)	130.6 (d)	144.8 (d)	130.6 (d)	136.7 (d)	198.2 (s)	44.1 (d)	132.5 (s)	159.9 (s)	159.9 (s)	132.5 (s)	33.9 (t)	84.7 (t)		21.0 (q)
16	123.3 (d)	142.5* (d)	129.3 (d)	133.7* (d)	133.7* (d)	129.3 (d)	142.5* (d)	123.3 (d)	38.5 (s)	187.3 (s)	157.9 (s)	132.7 (s)	132.7 (s)	157.9 (s)	43.8 (t)	43.8 (t)		27.9 (q)
17	129.6 (d)	142.0 (d)	130.1 (d)	133.3 (d)	132.2 (d)	130.5 (d)	141.2 (d)	124.6 (d)	134.9 (s)	189.7 (s)	145.1 (s)	133.1 (s)	130.8 (s)	139.6 (s)	160.0 (d)	20.9 (q)		19.4 (q)
20	122.8 (d)	142.2* (d)	128.6 (d)	137.4* (d)	137.4* (d)	128.6 (d)	142.2* (d)	122.8 (d)	39.5 (s)	183.8 (s)	158.9 (s)	131.9 (s)	131.9 (s)	158.9 (s)	45.3 (t)	45.3 (t)		19.7 (q)

^a Chemical shifts are in parts per million from external Me₄Si. ^b Multiplicities are in parentheses: s = singlet, d = doublet, t = triplet, q = quartet. Resonances within a spectrum which are labeled with an equivalent number of asterisks have interchangeable assignments. ^c Assignments of chemical shifts for ions 15a and 15b are tentative. ^d Phenyl shifts at (¹³C) δ 134.3, 131.4, 130.1, and 128.1.



14 might be responsible for this protonation at C-10 since fluorine at C-16 might be deactivating the C-9 position up to some extent for protonation. Ionization of **14** at $-90\text{ }^\circ\text{C}$ with the Lewis acid

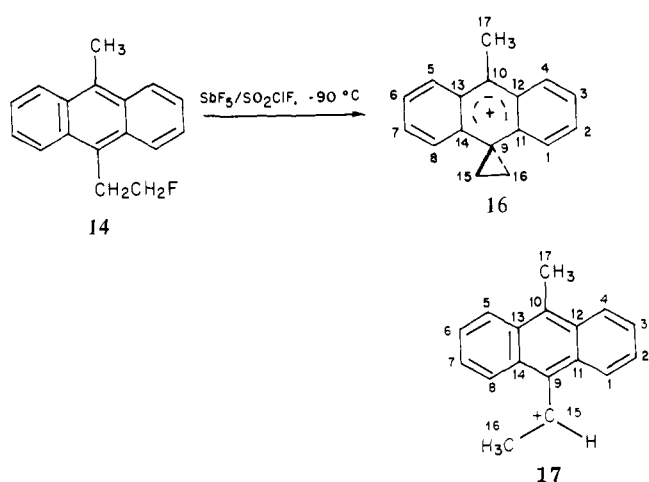


SbF₅/SO₂ClF, however, gave a reddish brown solution. The ¹H and ¹³C spectrum (Figure 2a) of this solution showed it to be the 9-(α-ethylene)-10-methylanthracenium ion (**16**). No rearranged benzylic ion **17** is present. The 200-MHz ¹H NMR resonances of ion **16** are listed in Table I. The symmetrical cyclopropane methylene protons are at δ 2.8 and the C-10, methyl group at δ 3.0, and H₄, H₅ and H₂, H₇ are at δ 8.2 and 7.7, respectively. The remaining two resonances at δ 7.3 and 7.1 are assigned to H₃, H₆ and H₁, H₈. The ¹³C spectrum of ion **16** is shown in Figure 2a with assignments in Table II. The most deshielded peak at δ(¹³C) 187.3 is C-10. Another low-field signal at δ(¹³C) 157.9 is assigned to C-11, C-14. The proton-coupled spectrum enabled assignments of C-12, C-13 at δ(¹³C) 132.7, the spirocarbon C-9 at δ(¹³C) 38.5, the cyclopropane methylene carbons C-15, C-16 at δ(¹³C) 43.8, and the methyl group at δ(¹³C) 19.4. The additional two peaks at δ(¹³C) 142.5 and 133.7 are those of the C-2, C-7, and C-4, C-5 carbons affected by the delocalized positive charge. The remaining peaks at δ(¹³C) 129.3 and 123.3 are tentatively assigned to C-3, C-6 and C-1, C-8. Allowing the solution temperature to rise up to $-65\text{ }^\circ\text{C}$, ion **16** rearranges completely to ion **17** (see Figure 2b) again due to the opening of the cyclopropane ring of ion **16** followed by a 1,2-hydride shift. Further warming of the ion solution resulted in complete decomposition giving polymeric material. The structure of ion **16** is further proved by its independent preparation from alcohol **12a** which ionized in SbF₅/SO₂ClF at $-90\text{ }^\circ\text{C}$. The yellowish brown solution gave a ¹³C spectrum (Figure 2c) which is identical with that obtained from fluoride **14**. Similarly, the structure of ion **17** was proved by its preparation from alcohol **18**²¹ which was ionized in FSO₃H/SO₂ClF at $-78\text{ }^\circ\text{C}$. The ¹H NMR (Table I) and ¹³C NMR (Figure 2d and Table II) spectra of ion **17** are very clean and easily assigned. Once again like ion **9** this ion **17** is unsymmetrical, showing 17 signals in the ¹³C spectrum. The proton-coupled spectrum of ion **17** made it possible to assign the most deshielded resonance at δ(¹³C) 189.7 to C-10 and the peak at δ(¹³C) 161.0 to

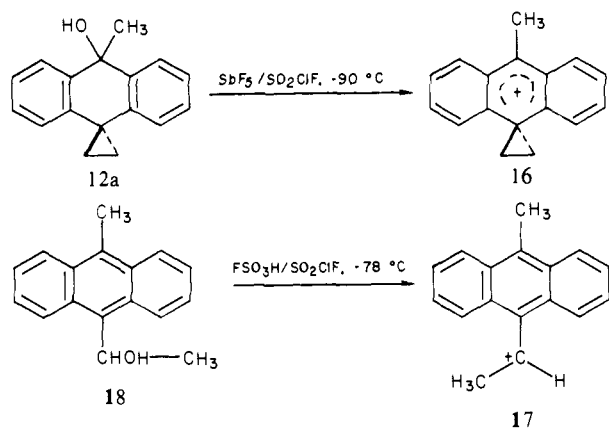
(19) A high yield of alcohol **12a** was obtained by reacting ketone **10c** with methylolithium and refluxing it overnight as compared to refluxing **10c** for 3 days with methylmagnesium bromide as reported by Rosenfield.²⁰

(20) Eynon, J.; LaFauci, R.; Rosenfield, S. M. *Org. Prep. Proced. Int.* **1979**, *11*, 71-6.

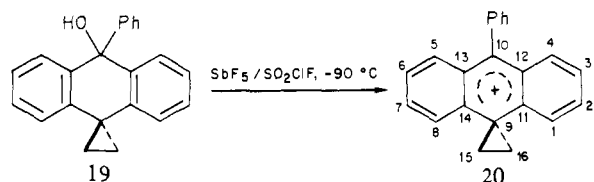
(21) Alcohol **18** was prepared by a method similar to that used for alcohol **11**¹⁷ (see Experimental Section).



C-15. The remaining peaks in the spectrum were tentatively assigned, similarly as in ion 9 (see Table II). It is significant to note here that C-10 is more deshielded than C-15, which is due to the substituent effect of the methyl group at this carbon and also probably due to more positive charge delocalized into the ring.



For comparison we also prepared the 9-(α -ethylene)-10-phenylanthracenium ion (20) from its corresponding tertiary spiro alcohol 19.²² The ^1H and ^{13}C NMR data of ion 20 are tabulated in Tables I and II, respectively.



Conclusion

In summary, the direct observation of the 9- α -ethyleneanthracenium ion (3) and the 9-(α -ethylene)-10-methylanthracenium ion (16) under stable ion conditions from their 9- β -fluoroethylanthryl precursors 7 and 14 and their ^1H and ^{13}C NMR spectroscopic study proves the formation of these symmetrically bridged ions via anthryl participation. These ions are identical with those prepared by Ebersson and Winstein's method from spirocyclopropyl precursors, such as 10 and 12a. Our results are in accord with and fully support Winstein's original conclusions reached in solvolytic studies for the involvement of these symmetrically bridged ions as reaction intermediates in the solvolysis of 9- β -anthrylethyl systems.

Experimental Section

All the boiling and melting points are uncorrected. Melting points were recorded on a Metler FPI apparatus. All the proton spectra of

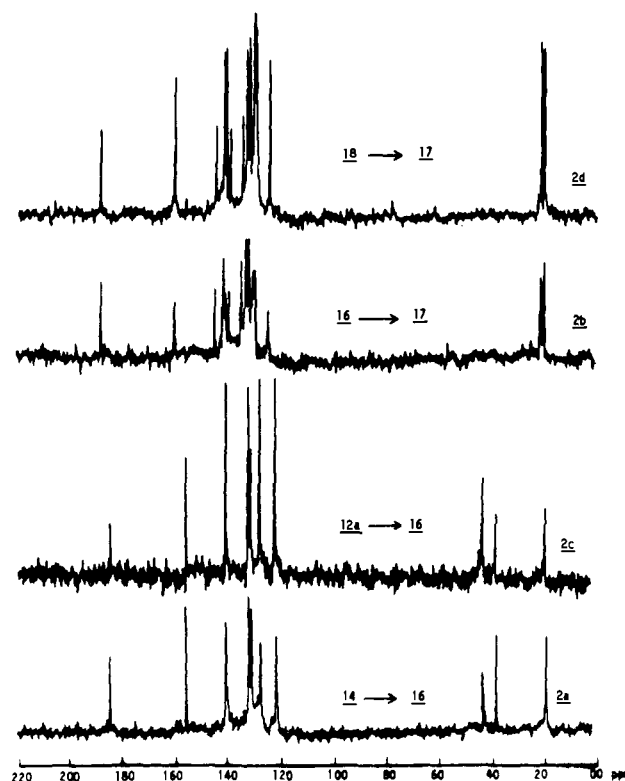
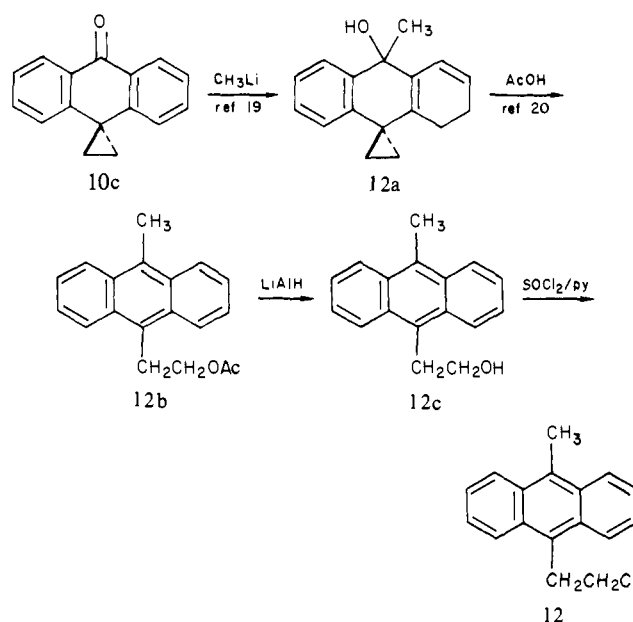


Figure 2. Carbon-13 spectra of ions 16 and 17.

Scheme II



starting precursors and ions, unless specified, were recorded on a Varian XL-200 superconducting spectrometer. All carbon-13 spectra were recorded on a Varian FT-80 spectrometer equipped with a multinuclear broad-band probe and variable-temperature controller. All the compounds used in this study were prepared in our laboratory by literature procedures and analyzed by spectroscopic techniques except for a few starting precursors such as anthrone, 9-bromoanthracene, 9-anthraldehyde, and 10-methylanthracene-9-carboxaldehyde which were obtained from Aldrich Chemical Co. All proton and carbon-13 NMR chemical shifts are with reference to external tetramethylsilane. FSO_3H and SbF_5 used in this study were freshly distilled before use.

Preparation of Alcohol 12c. Acetate 12b²⁰ (3 g, 10.8 mmol) was dissolved in 50 mL of dry THF under nitrogen atmosphere and (15 mmol) lithium aluminum hydride was added slowly. The reaction mixture was refluxed for 0.5 h. The cold reaction mixture was poured into ice cold water and extracted with (2 \times 100 mL) chloroform. The chloroform layer was washed with brine and dried over anhydrous MgSO_4 .

(22) Alcohol 19 was prepared from ketone 10c and phenyllithium (see Experimental Section).

Removal of solvent gave a solid residue which was recrystallized with hexane-chloroform mixture to give pure alcohol **12c** (2.3 g, 90.1% yield): mp 117.1 °C; ^{13}C NMR (CDCl_3) $\delta_{(13\text{C})}$ 14.1, 30.9, 63.2, 124.7, 124.8, 125.2, 125.3, 128.3, 129.5, 129.8, 129.9.

Preparation of Chlorides 4 and 12. Alcohol **4a** or **12c** (10 mmol) was dissolved in 100 mL of dry ether having 1 mL of pyridine. Thionyl chloride (10 mL) in 15 mL of dry ether was added slowly, and the reaction mixture was refluxed overnight. Cold reaction mixture was poured into ice water and extracted with chloroform (2×200 mL). The organic layer was successively washed with water, NaHCO_3 solution, and brine solution and dried over anhydrous MgSO_4 . The crude product was purified by column chromatography (silica gel, hexane:chloroform) to give pure **4** (1.8 g, 75.6% yield), mp. 150.5 °C, or **12** (1.5 g, 60% yield), mp 139.5 °C. ^{13}C NMR (CDCl_3) for **4**: $\delta_{(13\text{C})}$ 31.6, 43.4, 123.6, 123.9, 125.0, 125.7, 126.3, 126.4, 127.1, 129.3. ^{13}C NMR (CDCl_3) for **12**: $\delta_{(13\text{C})}$ 14.2, 31.6, 43.5, 124.2, 124.8, 125.6, 125.7, 127.7, 129.6, 129.9, 130.4.

Preparation of Fluorides 7 and 14. These fluorides were made from the corresponding alcohols **4a** and **12c** by using Middleton's method.¹² Alcohol **4a** or **12c** (10 mmol) was dissolved in 25-30 mL of dry CH_2Cl_2 at -78 °C under dry nitrogen atmosphere. Diethylaminosulfur trifluoride (12 mmol) was added, and the reaction mixture was warmed up to room temperature. The mixture was stirred for additional 30 h. at room temperature and then poured into ice cold water and extracted with (2×50 mL) CH_2Cl_2 . The methylene chloride layer was washed successively twice with water, once with NaHCO_3 solution, and finally with brine solution. Drying over anhydrous MgSO_4 and removal of solvent gave a solid residue, which was purified by column chromatography (silica gel, hexane) to give pure **7** as yellow niddles (1.5 g, 68.1% yield), mp 80-82 °C, or pure **14** as yellow flakes (1.6 g, 76.2% yield), mp 165-67 °C. ^{13}C NMR (CDCl_3) for **7**: $\delta_{(13\text{C})}$ 28.7 ($J_{\text{C-F}} = 21.3$ Hz), 83.1

($J_{\text{C-F}} = 171.6$ Hz), 123.8, 124.8, 125.9, 126.8, 129.2, 130.2, 131.4, 133.4. ^{13}C NMR (CDCl_3) for **14**: $\delta_{(13\text{C})}$ 14.2, 28.9 ($J_{\text{C-F}} = 20.9$ Hz), 83.2 ($J_{\text{C-F}} = 171$ Hz), 124.4, 124.8, 125.5, 129.9, 130.0.

Preparation of Alcohol 19. Spiro ketone **10c** (2 g, 9.1 mmol) in dry THF (50 mL) under an N_2 atmosphere was reacted with phenyllithium (12 mmol). The reaction mixture was refluxed overnight. The cold reaction mixture was poured into ice cold water, extracted with (2×100 mL) ether, and dried over anhydrous MgSO_4 . Removal of solvent gave a yellowish crystalline solid which was recrystallized with hexane-chloroform mixture to give pure **19** (2 g, 79% yield); mp 180.7 °C; ^{13}C NMR (CDCl_3) $\delta_{(13\text{C})}$ 17.6, 22.0, 25.5, 75.1, 121.2, 126.0, 126.2, 126.5, 127.2, 127.7, 127.9, 138.0, 142.5, 147.9.

Preparation of Alcohol 18. 10-Methylanthracene-9-carboxaldehyde (10 mmol) was dissolved into 100 mL of dry THF and methylolithium (12 mmol) was added slowly. The reaction mixture was refluxed overnight. The cold reaction mixture was poured into ice water and extracted with chloroform (2×100 mL), washed with brine solution, and evaporated. The solid residue was recrystallized with hexane-chloroform mixture to give pure alcohol **18** (2.1 g, 89% yield): mp 140 °C; ^{13}C NMR (CDCl_3) $\delta_{(13\text{C})}$ 14.4, 23.5, 67.1, 124.6, 124.8, 125.2, 125.4, 128.4, 129.9, 130.3, 134.5.

General Procedure for the Preparation of Ions. All the ions were prepared in the usual manner in the NMR tubes by adding 200-250 mg of the neat solid in small portions to a well-stirred solution of approximately 0.5 mL of acid in 2 mL of SO_2ClF or SO_2 at -78 °C or lower temperature. The NMR tube is well stirred on Vortex and placed at low temperature into the NMR probe to record its spectrum.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

α -Amino Carbanions via Formamidines.¹ Alkylation of Pyrrolidines, Piperidines, and Related Heterocycles

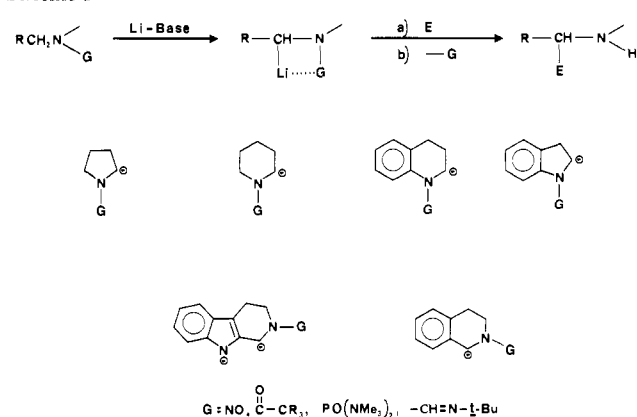
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Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Received October 3, 1983. Revised Manuscript Received January 7, 1984

Abstract: α -Metalation of piperidine, pyrrolidine, hexahydroazepine, 1,3-thiazolidine, and 1,3-thiazane has been accomplished via their *N-tert*-butylformamidines derivatives. Alkylation of these α -amino carbanions via their lithio or cuprate derivatives leads to good yields of α -substituted heterocycles. Similarly, 1,2,5,6-tetrahydropyridine metalates at the 2 position, but alkylates at the 4 position. Reduction leads to 4-substituted piperidines. Evidence is presented to show that electron-transfer processes occur when the C-Li bond is not orthogonal to the plane of the formamidines moiety.

Although alkylation of the α carbanion of amino derivatives using an electronically modified nitrogen function is now a well-known process (Scheme I),² several serious limitations to this methodology still exist. For example, the extensive studies by Seebach using nitrosoamines³ are affected by the potential health hazards in employing these substances, while metalation-alkylation of hindered amides studied by Beak^{4a} and Seebach^{4b,c} is limited to certain substituents and, on occasion, to harsh conditions to regenerate the amine after alkylation. Furthermore, evidence is mounting that the dipole-stabilized anion intermediate requires that the carbon-lithium bond be orthogonal to the π system,^{4,5} which results in some serious side reactions leading to poor yields

Scheme I



(1) Part 8 on carbanions derived from formamidines. For previous reports on this work see: Meyers, A. I.; Fuentes, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 117, and references cited. See also: Meyers, A. I.; Fuentes, L. M.; Kubota, Y. *Tetrahedron Symp.*, in press.

(2) For a review on this subject, see: (a) Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275. (b) Beak, P.; Zajdel, W. J.; Reitz, D. B. *Ibid.*, in press.

(3) Seebach, D.; Enders, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 15.

(4) (a) Beak, P.; Zajdel, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 1010. (b) Seebach, D.; Lohman, J. J.; Syfrig, M. A.; Yoshifuji, M. *Tetrahedron* **1983**, *39*, 1963. (c) Schlecker, R.; Seebach, D. *Helv. Chim. Acta* **1977**, *60*, 1459.

(5) Seebach, D.; Wykpiel, W.; Lubosch, W.; Kalinowski, H. O. *Helv. Chim. Acta* **1978**, *61*, 3100.

and/or mixtures of products. Specifically, the alkylation using alkyl halides of simple *unsubstituted* heterocycles such as piperidine, pyrrolidine, and perhydroazepine give poor (<20%) yields of alkylation when hindered amides or formamidines are used as the N-activating groups. Thus, as shown in Scheme II, the