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: Eberson 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–SO₂ 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 Cram[2] and studied extensively.[3] The involvement of σ-bridged ethylenebenzenium ion (**1**) and ethylenenaphthalenium ion (**2**) was a question of controversy[4] but

1   **2**
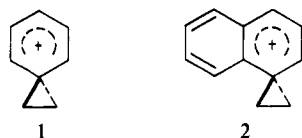
is now well established helped by direct observation of long-lived ions under stable ion conditions.[5,6] Similar participation by an anthryl group has been proposed by Winstein et al. in the solvolysis and deuterium-scrambling studies[7] involving 9-α-ethyleneanthracenium ion (**3**) as an intermediate. Eberson and Winstein were able to prepare and study **3** by ¹H NMR spectroscopy under stable ion[8] 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-ethylanthracene derivatives under stable ion conditions

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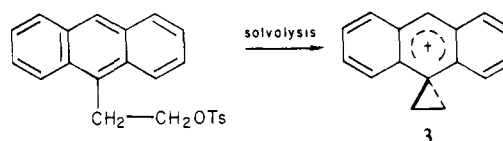
remained a challenge. In continuation of our studies of ethylenebenzenium and naphthalenium ions we now wish to report our success to achieve this goal in directly preparing the elusive 9-α-ethyleneanthracenium ion **3** and its substituted homologues and report their study by proton and carbon-13 NMR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

X = Cl, Br   **3**
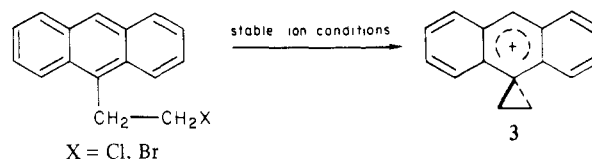
Results and Discussion

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 $\delta_{(^{13}C)}$ 38.1, 33.2, and 44.8 are assigned to C-10, C-15, and C-16, respectively. The most deshielded peak at $\delta_{(^{13}C)}$ 195.5 is assigned to C-9. Another low-field peak at $\delta_{(^{13}C)}$ 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]

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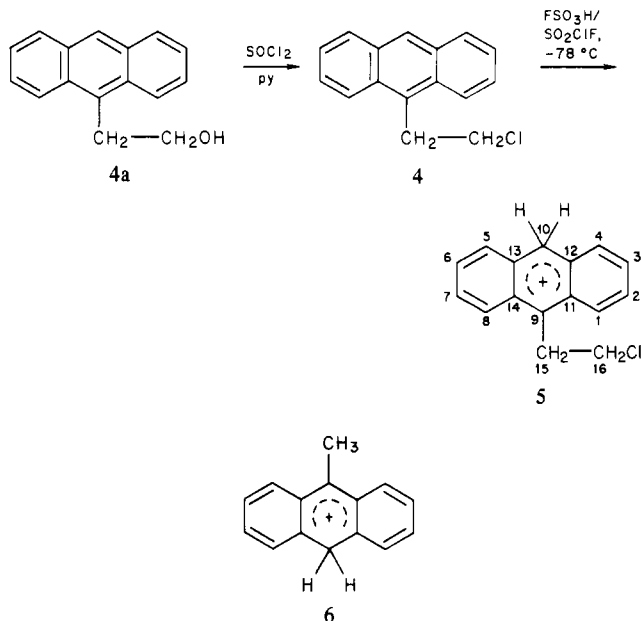
(4) Brown, H. C.; Morgan, K. J.; Chloupek, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 2137.

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

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

(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*, 208i.

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 FSO_3H/SO_2ClF or $HF-BF_3$, a nonoxiding 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 $\delta_{(^{13}C)}$ 197.4 is assigned to C-9. The signals at $\delta_{(^{13}C)}$ 33.4 (a doublet, $J_{C-F} = 19.7$ Hz) and 84.5 (a doublet, $J_{C-F} = 175.1$ Hz) are assigned to C-15 and C-16, respectively. The C-10 methylene is at $\delta_{(^{13}C)}$ 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
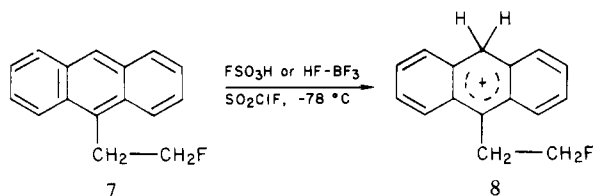
redish brown solution whose ^1H and ^{13}C NMR spectra showed it to be the elusive 9-α-ethyleneanthracenium ion (**3**) with a trace amount of benzylic ion **9** also present (Figure 1a). The 200-MHz ^1H spectrum of ion **3** shows six sets of peaks which are assigned as in Table I. In this ion C-10 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 assignments[13] given in Table II. The most deshielded signal at $\delta_{(^{13}C)}$ 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 $\delta_{(^{13}C)}$ 160.0 and 131.9, as well as of the spiro carbon C-9

(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 intencities, and (c) comparison of ^{13}C spectrum to protonated anthracenes.[11]

and symmetrical cyclopropane methylenes C-15, C-16 at $\delta_{(^{13}C)}$ 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 $\delta_{(^{13}C)}$ 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 $\delta_{(^{13}C)}$ 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 $\delta_{(^{13}C)}$ 40.7 (C-9, spiro carbon) and $\delta_{(^{13}C)}$ 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**.
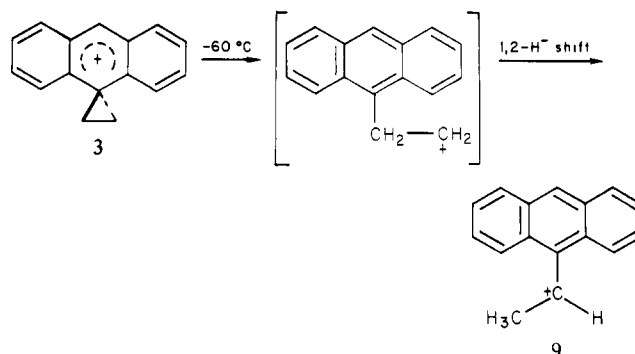
The presence of observed traces of ion **9** in the -90 °C spectrum of ion **3** may also be explained in the same way due to local overheating during preparation of ion from precursor **7**. The ^{13}C spectrum (Figure 1b) shows 16 signals which indicates that ion **9** is unsymmetrical. In fact, this is expected in the frozen out form of ion **9**. The most deshielded signal at $\delta_{(^{13}C)}$ 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 $\delta_{(^{13}C)}$ 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 $\delta_{(^{13}C)}$ 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 Eberson and Weinstein's procedure, i.e., from precursor spiro-cyclopropyl alcohol **10**. Precursor **10** was prepared by a series of reactions as shown in Scheme I. Ionization of alcohol **10** in SbF_5/SO_2ClF 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**.

(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

	proton chemical shifts[a] and multiplicities[b]											
ions	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_{10}	H_{15}	H_{16}	others
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 Me_4Si. [b] Multiplicities are in parentheses: s = singlet, d = doublet, t = triplet, q = quartet, br = broad.
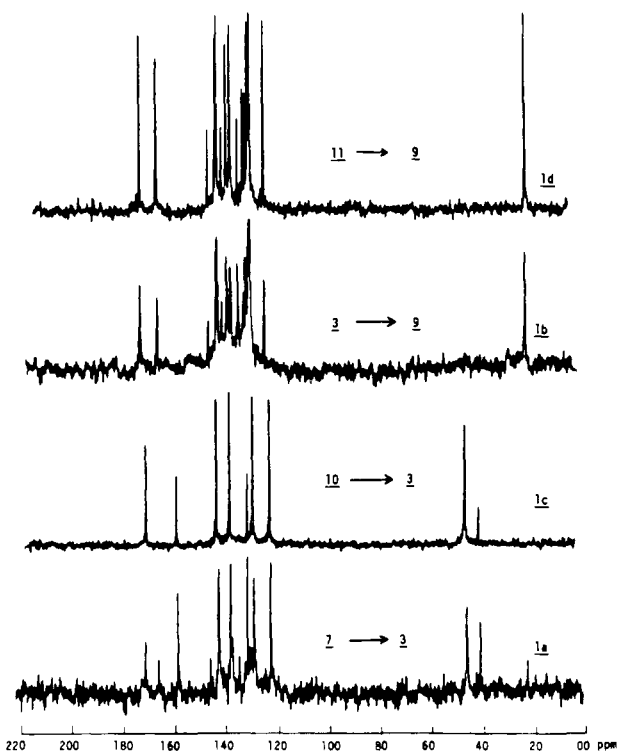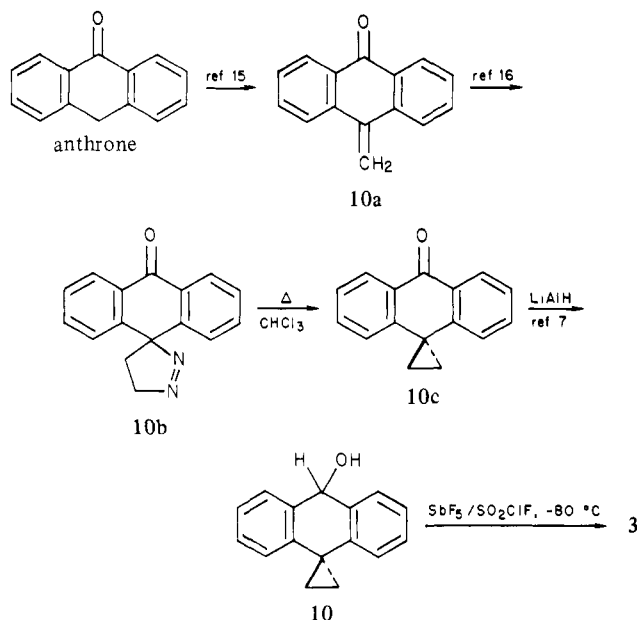

Figure 1. Carbon-13 spectra of ions 3 and 9.

Similarly, structure of ion **9** was further proved by preparing it independently from benzylic alcohol **11**.[17] Ionization of **11** in FSO_3H/SO_2ClF at −78 °C gave a clear yellowish red solution. The ^{13}C 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 H_{16}. H_{10} and H_{15} 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.
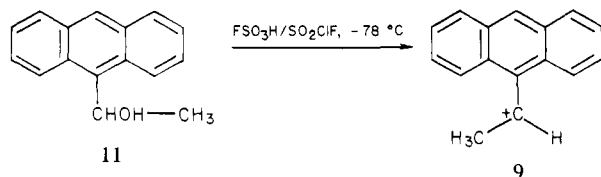
Preparation of 9-(α-Ethylene)-10-Methylanthracenium Ion (16).
The preparation of this ion was carried out from 9-(β-chloro-

(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 Rosenfield[20] using a tenfold excess of CH_2N_2. We were also able to isolate the intermediate compound **10b** which was confirmed by its ^1H and ^{13}C NMR data. ^1H NMR ($CDCl_3$) 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). ^{13}C NMR ($CDCl_3$) δ_{13C} 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.

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 SbF_5, FSO_3–SbF_5, or HF-SbF_5 at −78 °C or lower temperature gave a dark brown solution, ^{13}C spectrum of which showed very broad signals. This may again be due to oxidation of the aromatic ring by SbF_5 to give radical cation. Addition of **12** to a solution of FSO_3H/SO_2ClF or $HF:BF_3/SO_2ClF$ at −90 °C on the other hand resulted in the protonation of the aromatic ring to give ion **13**. The ^{13}C spectrum of this ion shows eleven resonances. The most deshielded signal at $\delta_{(13C)}$ 200.8 is that of C-10. The next lower field signal at $\delta_{(13C)}$ 154.9 is assigned to C-11, C-14. The proton-coupled spectrum enabled assignments for C-12, C-13 at $\delta_{(13C)}$ 132.8 and for C-9, C-15, C-16, and C-17 at $\delta_{(13C)}$ 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 ^{13}C 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 FSO_3H/SO_2ClF at −80 °C gives protonation at C-9 to form ion **15a** while in the nonoxidizing superacid HF–BF_3 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 ^{13}C 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

(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

carbon-13 chemical shifts[a] and multiplicities[b]

ions	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 [J_{C-F} = 19.7]	84.5 [J_{C-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)	20.6 (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)	21.0 (q)
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)	27.9 (q)
15b[c]	136.7 (d)	130.6 (d)	144.8 (d)	130.6 (d)	130.6 (d)	144.8 (d)	142.5* (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)	19.4 (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)	19.7 (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)	133.1 (s)	139.6 (s)	160.0 (s)	20.9 (q)	19.7 (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)	d

[a] Chemical shifts are in parts per million from external Me$_4$Si. [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 (^{13}C) δ 134.3, 131.4, 130.1, and 128.1.

CH$_3$ / CH$_2$CH$_2$Cl → FSO$_3$H/SO$_2$ClF, -78 °C → CH$_3$ / H CH$_2$CH$_2$Cl

12   13
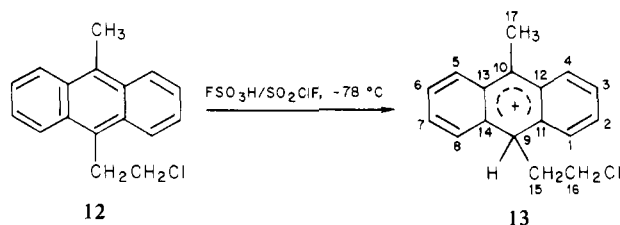
14 might be responsible for this protonation at C-10 since fluorine at C-16 might be deactivating the C-9 position up to some extent for protonation. Ionization of **14** at -90 °C with the Lewis acid

CH$_3$ / CH$_2$CH$_2$F → HF-BF$_3$, -90 °C → CH$_3$ / H CH$_2$CH$_2$F   +

14   15a

H CH$_3$ / CH$_2$CH$_2$F

15b
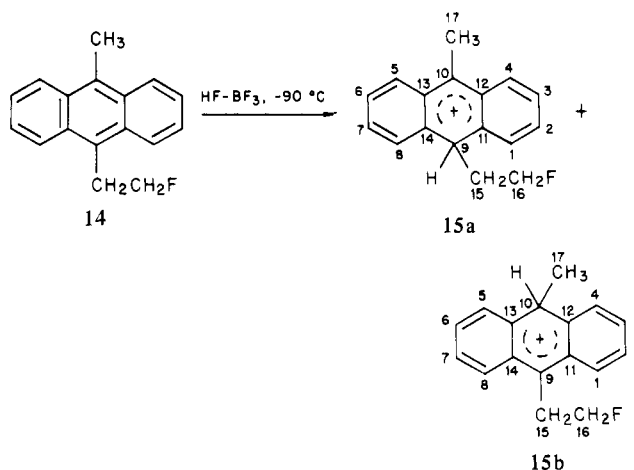
SbF$_5$/SO$_2$ClF, however, gave a reddish brown solution. The ^{1}H and ^{13}C spectrum (Figure 2a) of this solution showed it to be the 9-(α-ethylene)-10-methylanthracenium ion (**16**). No rearranged benzylic ion **17** is present. The 200-MHz ^{1}H NMR resonances of ion **16** are listed in Table I. The symmetrical cyclopropane methylene protons are at δ 2.8 and the C-10, methyl group at δ 3.0., and H$_4$, H$_5$ and H$_2$, H$_7$ are at δ 8.2 and 7.7, respectively. The remaining two resonances at δ 7.3 and 7.1 are assigned to H$_3$, H$_6$ and H$_1$, H$_8$. The ^{13}C spectrum of ion **16** is shown in Figure 2a with assignments in Table II. The most dishielded peak at $\delta_{(^{13}C)}$ 187.3 is C-10. Another low-field signal at $\delta_{(^{13}C)}$ 157.9 is assigned to C-11, C-14. The proton-coupled spectrum enabled assignments of C-12, C-13 at $\delta_{(^{13}C)}$ 132.7, the spirocarbon C-9 at $\delta_{(^{13}C)}$ 38.5, the cyclopropane methylene carbons C-15, C-16 at $\delta_{(^{13}C)}$ 43.8, and the methyl group at $\delta_{(^{13}C)}$ 19.4. The additional two peaks at $\delta_{(^{13}C)}$ 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 $\delta_{(^{13}C)}$ 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 °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 SbF$_5$/SO$_2$ClF at -90 °C. The yellowish brown solution gave a ^{13}C 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 FSO$_3$H/SO$_2$ClF at -78 °C. The ^{1}H NMR (Table I) and ^{13}C 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 ^{13}C spectrum. The proton-coupled spectrum of ion *17* made it possible to assign the most deshielded resonance at $\delta_{(^{13}C)}$ 189.7 to C-10 and the peak at $\delta_{(^{13}C)}$ 161.0 to

(19) A high yield of alcohol **12a** was obtained by reacting ketone **10c** with methyllithium 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. Proceed. Int.* **1979**, *11*, 71-6.

(21) Alcohol **18** was prepared by a method similar to that used for alcohol **11**[17] (see Experimental Section).
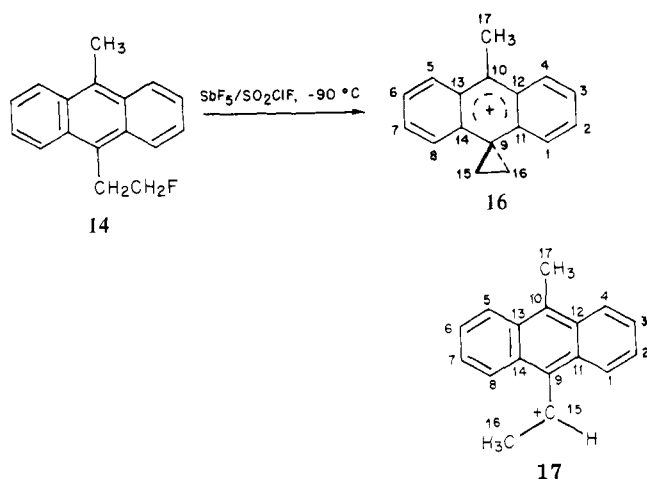
C-15. The remaining peaks in the spectrum were tentatively assigned, similarly as in ion **9** (see Table II). It is significant to note here that C-10 is more deshielded than C-15, which is due to the substituent effect of the methyl group at this carbon and also probably due to more positive charge delocalized into the ring.
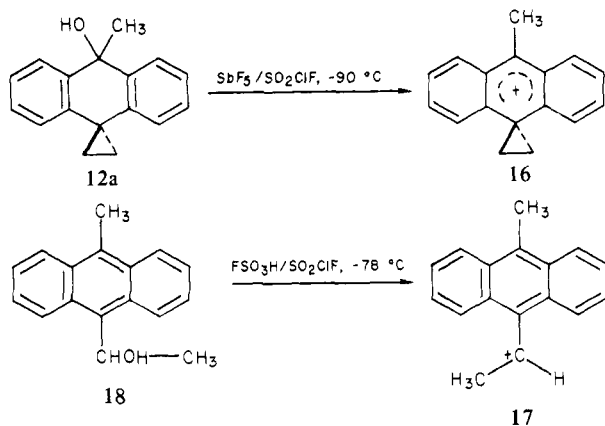
For comparison we also prepared the 9-(α-ethylene)-10-phenylanthracenium ion (**20**) from its corresponding tertiary spiro alcohol **19**.[22] The ^1H and ^{13}C NMR data of ion **20** are tabulated in Tables I and II, respectively.
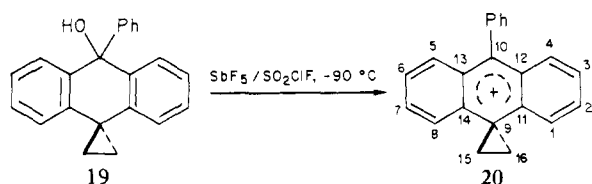
Conclusion

In summary, the direct observation of the 9-α-ethylene-anthracenium ion (**3**) and the 9-(α-ethylene)-10-methyl-anthracenium 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 Eberson 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
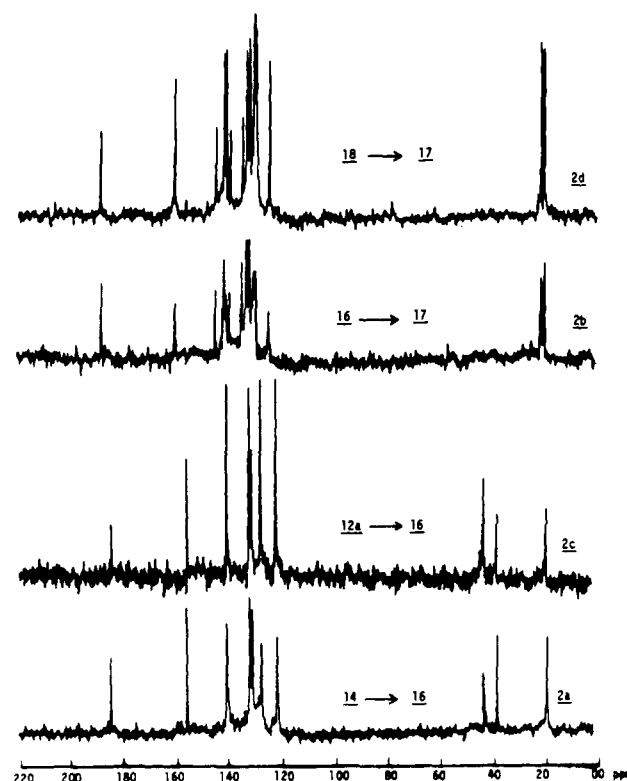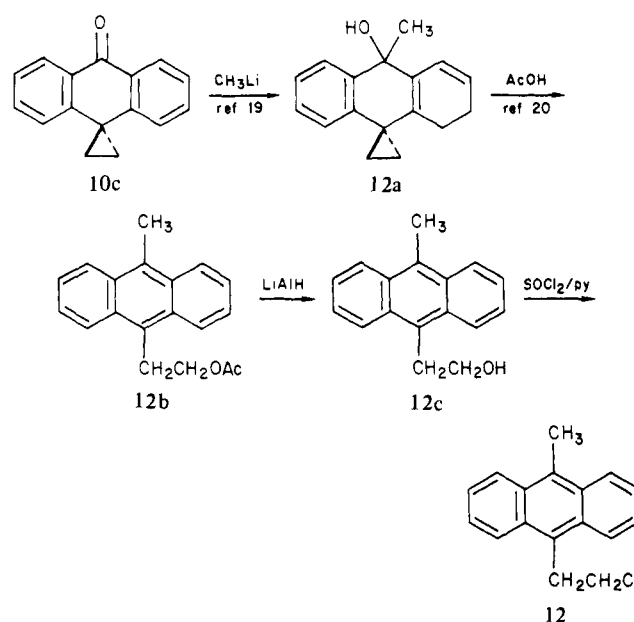
(22) Alcohol **19** was prepared from ketone **10c** and phenyllithium (see Experimental Section).

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 **12b**[20] (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 × 100 mL) chloroform. The chloroform layer was washed with brine and dried over anhydrous $MgSO_4$.

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$_3$) $\delta_{(^{13}C)}$ 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**: $\delta_{(^{13}C)}$ 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**: $\delta_{(^{13}C)}$ 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$_2$Cl$_2$ 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$_2$Cl$_2$. The methylene chloride layer was washed succesively 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**: $\delta_{(^{13}C)}$ 28.7 ($J_{C–F}$ = 21.3 Hz), 83.1 ($J_{C–F}$ = 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**: $\delta_{(^{13}C)}$ 14.2, 28.9 ($J_{C–F}$ = 20.9 Hz), 83.2 ($J_{C–F}$ = 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$_3$) $\delta_{(^{13}C)}$ 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 methyllithium (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$_3$) $\delta_{(^{13}C)}$ 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$_2$ClF 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.

α-Amino Carbanions via Formamidines.[1] Alkylation of Pyrrolidines, Piperidines, and Related Heterocycles
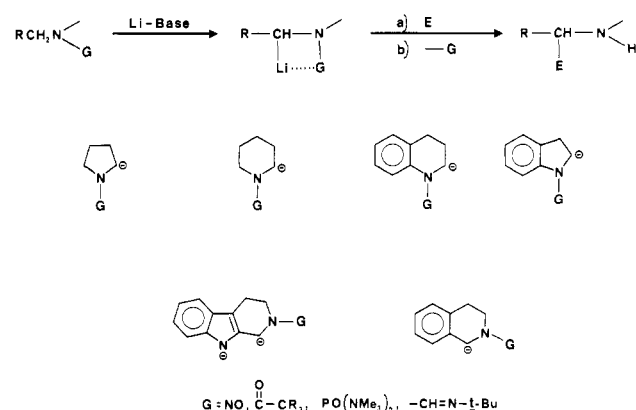
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Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Received October 3, 1983. Revised Manuscript Received January 7, 1984

Abstract: α-Metalation of piperidine, pyrrolidine, hexahydroazepine, 1,3-thiazolidine, and 1,3-thiazane has been accomplished via their *N-tert*-butylformamidine 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 formamidine 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 nitrosoamines[3] 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

$$G = NO, \ \overset{\overset{\displaystyle O}{\|}}{C}-CR_3, \ PO(NMe_2)_2, \ -CH=N-\underline{t}\text{-Bu}$$

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

(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.