for **Y-2**], and 6.54 [aryl H] in the ratio of 12:3:6[29]:4; **Y-2**, assigned structure 4 [R = CH_3, Ar = 2,6-dimethyl-4-methoxyphenyl]: four singlets at 2.05 [$ArCH_3$], 3.12 [NCH_3], 3.74 [CH_3O, overlapping with a band for **X-2**], and 6.49 [aryl H] in the ratio 12:6:6[29]:4.) The ratio of acetylene **9**, MeTAD, **X-2**, and **Y-2** was 42:34:12:12.

Reaction of Bis(2,6-dimethyl-4-methoxyphenyl)acetylene with PhTAD. To a solution of 20.5 mg (0.07 mmol) of bis-(2,6-dimethyl-4-methoxyphenyl)acetylene in 4 mL of CH_2Cl_2 was added 26.8 mg (0.153 mmol) of PhTAD in 4 mL of CH_2Cl_2. The solution turned dark red. After stirring for 5 days at room temperature, the dark red solution was directly applied to a preparative TLC plate with CH_2Cl_2 as eluent (R_f = 0.58), affording 8.4 mg (26%) of urazole **10(X-1)**: mp 153.5 °C (hexane); IR (CHCl3, cm^{-1}) 3000–2820 (m), 1780 (w), 1733 (vs), 1600 (s), 1325 (m), 1315 (m), 1220 (m), 1192 (m), 1140 (s), 1068 (w); ^1H NMR ($CDCl_3$, Me_4Si, ppm) 2.37 (s, 12 He, 3.77 (s, 6 H), 6.59 (s, 4 H), 7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si, ppm) 21.22, 55.07. 113.75, 118.82, 125.37, 128.79, 129.27, 131.61, 138.63, 140.88, 156.01, 160.73; UV (CH_3CN, nm) λ_{max} 267 (log e, 4.16).

Anal. Calcd for $C_{28}H_{27}N_3O_4$ (Found): C, 71.62 (71.35); H, 5.80 (6.02); N, 8.95 (8.77).

Compound **X-1** was unchanged upon heating at 160 °C for 30 min; at higher temperature it decomposed. Compound **X-1** does not undergo further reaction with PhTAD.

Examination of the original reaction solution by NMR showed bands for urazole **X-1** (described above) and bands at 2.17 (s, $ArCH_3$), 3.76 (s, $ArOCH_3$), 6.50 (s, ArH), product **Y-1**. The peaks of *N*-phenyl group overlapped with those of PhTAD and urazole **X-1**. Efforts to isolate this second compound were unsuccessful.

(29) Overlapping peak, estimated number. (*Note*: This is the only overlapping peak in this spectrum of 12 possible [11 observed] peaks, all singlets.)

Into an NMR tube were placed 6.5 mg (0.22 mmol) of bis-(2,6-dimethyl-4-methoxyphenyl)acetylene, 3.9 mg (0.023 mmol) of PhTAD, and 0.5 mL of CD_2Cl_2. After 6 h the ^1H NMR spectrum of the reaction mixture showed three singlets for the $ArCH_3$ protons of starting acetylene, urazole **X-1**, and the second product, **Y-1**, in a ratio of 21:2:4, corresponding to 3.3×10^{-3} mmol of **Y-1**. The solution was diluted with CH_2Cl_2; λ_{max} of **Y-1** 472.5 nm (log e 3.96).

Kinetics. Rates of reaction of PhTAD with the acetylene were measured in CH_2Cl_2 at 25 °C under pseudo-first-order conditions (PhTAD in excess), following the appearance of the bis(azomethine imine), **4a** or **4b**.

4b: Initial concentrations of PhTAD $\times 10^3$, bis(4-methoxyphenyl)acetylene $\times 10^4$, k_1 in M^{-1} s^{-1}; 9.95, 3.85, 0.0203; 10.3, 1.96, 0.0207; 10.2, 0.99, 0.0202; 4.87, 1.96, 0.0198; 6.74, 1.96, 0.0207 (average k_1 for the five runs, 0.0200 ± 0.0003 M^{-1} s^{-1}). **4a**: PhTAD $\times 10^3$, diphenylacetylene $\times 10^4$, k_1 in M^{-1} s^{-1}; 9.77, 5.91, 0.00315; 9.58, 5.91, 0.0303 (average k_1 = 0.00309 ± 0.00006 M^{-1} s^{-1}). **4b from the 1:1 adduct Z**: PhTAD $\times 10^2$, compound **Z** $\times 10^5$, k_3 in M^{-1} s^{-1}; 1.84, 2.54, 0.0232; 0.68, 3.11, 0.0244; 1.10, 2.64, 0.0220 (average k_3 for the three runs, 0.0232 ± 0.0008 M^{-1} s^{-1}).

Registry No. 1, 90461-05-5; **2**, 90461-06-6; **3b**, 2132-62-9; **4b**, 90461-07-7; **4c**, 90461-10-2; **4d**, 90461-09-9; **9**, 90461-11-3; **10(X-1)**, 90461-13-5; **10(X-2)**, 90461-12-4; **10(Z)**, 90461-08-8; PhTAD, 4233-33-4; MeTAD, 13274-43-6; 3-hexyne, 928-49-4; cyclooctyne, 1781-78-8.

Supplementary Material Available: X-ray data for **4b** (tables of atomic coordinates, final anisotropic thermal parameters, bond lengths, bond angles, dihedral angles); ^{13}C NMR assignments for **2**, **4b**, **4d**, **10(X-1)**: UV spectra for **3b** and **4b**; kinetics data for **3b** with PhTAD (10 pages). Ordering information is on any current masthead page.

Stable Carbocations. 255.[1] α-Ethylenehaloarenium Ions

George A. Olah,* Brij P. Singh, and G. Liang

Donald P. and Katherine B. Loker Hydrocarbon Research Institute—Department of Chemistry, University of Southern California, University Park—MC 1661, Los Angeles, California 90089

Received January 27, 1984

Ionization of a series of *p*-halogen-substituted phenylethyl chlorides **1a–c** under stable ion conditions gave via phenyl participation the corresponding 4-halo-α-ethylenebenzenium ions **2a–c**. The stability of ions **2a–c** is affected by the halogen atoms through their "back donation". Similarly, ionization of 9-(2-fluoroethyl)-10-bromoanthracene (**7**) gave 9-(α-ethylene)-10-bromoanthracenium ion **6** by similar anthryl group participation. Ionization of 1-(2-haloethyl)-4-bromonaphthalenes **11a,b**, however, even at −110 °C gave only the rearranged benzylic ion **12** without any detectable 4-bromo-α-ethylenenaphthalenium ion **10**.

Extensive study of the solvolysis of 2-arylethyl systems, notably by Cram, suggested involvement of aryl participation forming α-ethylenebenzenium ions ("phenonium ions") as the reaction intermediates.[2] These ions subsequently have been observed under long-lived stable ion conditions.[3] The degree of phenyl participation in the solvolytic reactions has been shown to be dependent on the substituents in the phenyl ring. Electron-releasing groups in the para position such as methoxy and methyl have been shown to enhance phenyl participation whereas electron-withdrawing groups such as NO_2, CF_3, etc., diminish such participation.[2] The influence of para substitution by halogen atoms on the phenyl ring is of particular interest in view of the opposing inductive and conjugative effects. Solvolysis of 2-(*p*-chlorophenyl)ethyl esters has been shown to involve some phenyl participation, as indicated by Hammett plots of log K_t against the σ value of the substituent.[4] Deviation from the straight-line plots was taken as a measure of phenyl participation. Halogens are considered to be electron-withdrawing groups due to their electronegativity but at the same time they also have nonbonded electron pairs, which are well-known for their stabilizing ability of carbenium ion centers through their "back donation" ability, especially in the case of fluorine. The degree of "back donation" was found to be dependent on the electronegativity of halogen atoms.[5]

(1) (a) For part 254, see: Olah, G. A.; Singh, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 3265. (b) Initital studies were carried out at Case Western Reserve University, Cleveland, OH.

(2) Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. "Carbonium Ions"; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 27.

(3) (a) Olah, G. A.; Singh, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 5168 and ref 2a,c–f cited therein. (b) Olah, G. A.; Singh, B. P. *Ibid.* **1984**, *106*, 3265.

(4) Harris, J. M.; Schadt, F. L.; Schleyer, P. v. R.; Lancelot, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 7508.

(5) Olah, G. A.; Mo, Y. K.; Halpern, Y. *J. Am. Chem. Soc.* **1972**, *94*, 3551.

0022-3263/84/1949-2922$01.50/0

Table I. ^{1}H NMR Parameters of Ions 2a–c

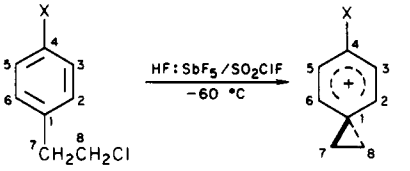
ions	proton chemical shifts[a] and multiplicities[b]		
	H_2, H_6	H_3, H_5	H_7, H_8
2a	8.7 (dd), J_{H-F} = 8.8 Hz	8.0 (dd), J_{H-F} = 10.0 Hz	4.6 (s)
2b	8.5 (d), J_{H-H} = 8 Hz	8.3 (d), J_{H-H} = 8 Hz	4.7 (s)
2c	8.4 (br, s)	8.4 (br, s)	4.7 (s)

[a] Chemical shifts are in parts per million with reference to Me_4Si. [b] Multiplicities are in parentheses, s = singlet, d = doublet, dd = doublet of a doublet, br broad.

Our continued interest in the study of halogenated carbocations leads us now to attempt (1) to prepare and study (by NMR spectroscopy) stable long-lived halogen substituted α-ethylenebenzenium ions as well as related ions such as naphthalenium and anthracenium ions and (2) to establish whether there is "back donation" by halogen atoms to stabilize these ions.

Results and Discussions

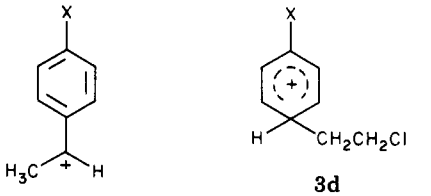
4-Halo-α-ethylenebenzenium Ions 2a–c. Ions **2a–c** were prepared by ionizing the corresponding (*p*-halophenyl)ethyl chlorides **1a–c**[6] in HF:SbF_5 (1:1 ratio)/SO_2ClF solution at −60 °C. The ^{1}H and ^{13}C NMR spectral



1a, X = F
b, X = Cl
c, X = Br

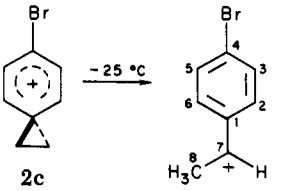
2a, X = F
b, X = Cl
c, X = Br

data of ions **2a–c** are given in Tables I and II, respectively. The proton NMR spectrum of ion **2a** showed a singlet at δ 4.6 for the symmetrical cyclopropane methylene protons H_7, H_8, one doublet of doublets at δ 8.0 assigned to H_3, H_5 protons, and another doublet of doublets at δ 8.7 which is assigned to H_2, H_6 protons. The ^{13}C NMR spectrum showed five sets of peaks. The most deshielded peak, a doublet centered at $\delta_{^{13}C}$ 182.1 (J_{C-F} = 294.8 Hz), is assigned to C_4. The other two sets of doublets centered at $\delta_{^{13}C}$ 175.2 (J_{C-F} = 18.0 Hz) and $\delta_{^{13}C}$ 122.4 (J_{C-F} = 22.4 Hz) are assigned to C_2, C_6 and C_3, C_5, respectively. Proton-coupled ^{13}C NMR spectra enabled us to assign the spiro carbon C_1 and symmetrical cyclopropane methylenes C_7, C_8 at $\delta_{^{13}C}$ 62.4 and 55.8. Similarly, the ^{1}H NMR spectrum of ion **2b** showed three sets of peaks. The singlet at δ 4.7 is assigned to the symmetrical cyclopropane methylene protons H_7, H_8. The most deshielded doublet at δ 8.5 is assigned to H_2, H_6 and another doublet at δ 8.3 is assigned to H_3, H_5 (Table I). The ^{13}C NMR spectrum of ion **2b** showed five peaks. Proton-coupled ^{13}C NMR spectra enabled assignments of C_2, C_6 and C_4 at $\delta_{^{13}C}$ 171.3 and 168.3. Another peak at $\delta_{^{13}C}$ 134.7 is assigned to C_3, C_5. Two peaks in the aliphatic region at $\delta_{^{13}C}$ 66.2 and 59.6 are assigned to spiro carbon C_1 and cyclopropane methylenes C_7, C_8. The proton NMR spectrum of ion **2c** showed a singlet at δ 4.7 for the cyclopropane methylene protons H_7, H_8 and a broad singlet for all H_2, H_6, H_3, H_5 at δ 8.4. The ^{13}C NMR spectrum of ion **2c** showed five peaks which are assigned to different carbons as shown in Table II. All the ions **2a–c** were found free of any rearranged open-chain secondary benzylic ions **3a– c**. Surprizingly, we also did not



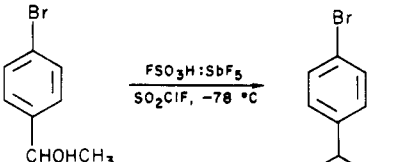
3a, X = F
3b, X = Cl
3c, X = Br

3d



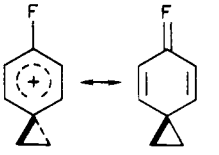
2c **3c**

observe any protonation on the benzene ring to give ion **3d**, although HF:SbF_5 is well-known for protonation of aromatic rings. Ion **2a** is stable up to 0 °C. Similarly, ion **2b** is stable up to −10 °C, but ion **2c** on the other hand rearranged completely at −25 °C to the corresponding benzylic ion **3c**. The ^{13}C NMR spectrum of ion **3c** showed eight peaks, which is expected for the frozen-out structure of this ion. The most deshielded peak at $\delta_{^{13}C}$ 224.8 is assigned to C_7. The proton-coupled spectrum enabled assignments of C_4, C_6, C_2, C_1 at $\delta_{^{13}C}$ 165.4, 152.3, 141.8, 139.7. Similarly, C_3, C_5, and C_8 are assigned at $\delta_{^{13}C}$ 137.7, 137.2, and 26.6. The structure of ion **3c** was further proved by preparing it independently from secondary alcohol **4**[7]



4 **3c**

and comparing the ^{13}C NMR spectra. The difference in stability of ions **2a–c** can be attributed to the difference in halogen atoms, back-donating ability which is known to decrease in the order of F > Cl ≫ Br.[5] In case of ion **2a** there is strong back donation by fluorine atom involving resonance structure **5** which means the positive charge is



2a **5**

partially delocalized on fluorine atom. This is evident by the deshielding effect on the chemical shift of C_4 in ions **2a–c** compared to the chemical shift of C_4 in neutral precursors **1a–c**. Formation of a partial double bond between C_4 and halogen atom will shield the chemical shift of C_4. The deshielding effect on chemical shift of C_4 follows the order of F < Cl < Br. The difference between the chemical shifts[8] of C_4 in ions **2a–c** and neutral precursors **1a–c** (Table II) was found to be 19.8, 35.2, and 38.0 ppm,

(6) Physical data of chlorides **1a–c** were compared to those given by Lee, K. H. *J. Chem. Soc., Perkin Trans. 2* **1973**, 693.

(7) Protiva, M.; Novak, L.; Sedivy, Z. *Collect. Czech. Chem. Commun.* **1962**, *27*, 2102.

(8) The purpose of comparing ^{13}C NMR shift differences, $\delta_{^{13}C}$ instead of ^{13}C NMR shifts of C_4, is to eliminate the influence of the inductive effect of halogen atoms.

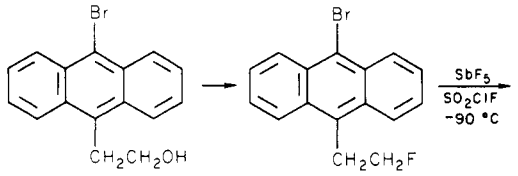
Table II. Carbon-13 Parameters of *p*-Halogen-Substituted α-Ethylenebenzenium Ions 2a–c and Their Neutral Precursors

	^{13}C chemical shifts[a] and multiplicities[b]						
	C_1	C_2, C_6	C_3, C_5	C_4	C_7	C_8	$(\delta_{^{13}C_4^+} - \delta_{^{13}C_4^n})$[c]
1a	134.2 (s)	130.8 (d), J_{C-F} = 8 Hz	115.8 (d), J_{C-F} = 21.2 Hz	162.3 (d), J_{C-F} = 244.7 Hz	38.7 (t)	45.5 (t)	
							19.8
2a	62.4 (s)	175.2 (d), J_{C-F} = 18 Hz	122.4 (d), J_{C-F} = 22.4 Hz	182.1 (d), J_{C-F} = 294.8 Hz	55.8 (t)	55.8 (t)	
1b	137.1 (s)	130.7 (d)	129.2 (d)	133.1 (s)	38.8 (t)	45.2 (t)	
							35.2
2b	66.2 (s)	171.3 (d)	134.7 (d)	168.3 (s)	59.6 (t)	59.6 (t)	
1c	137.6 (s)	132.2 (d)	131.1 (d)	121.3 (s)	38.9 (t)	45.2 (t)	
							38.0
2c	67.0 (s)	170.6 (d)	138.2 (d)	159.3 (s)	60.0 (t)	60.0 (t)	

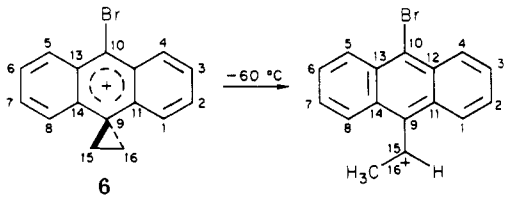
[a] Chemical shifts are in parts per million with reference to external Me_4Si. [b] Multiplicities are given in parentheses, s = singlet, d = doublet, t = triplet. [c] $\delta_{^{13}C_4^+} - \delta_{^{13}C_4^n}$ is the difference between the chemical shifts of C_4 in ionic and neutral substrates

respectively. This clearly indicates that there is a strong back donation by fluorine atom in ion **2a** and less back donation by chlorine in ion **2b**, and bromine probably has no or very little back donation in ion **2c**. The relative stability of the ion is also reflecting the same effect.

9-(α-Ethylene)-10-bromoanthracenium Ion (6). Ion **6** was obtained by slow addition of 9-(β-fluoroethyl)-10-bromoanthracene (**7**)[9,10] to a solution of SbF_5 in SO_2ClF

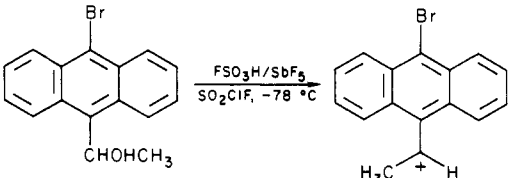


7a 7



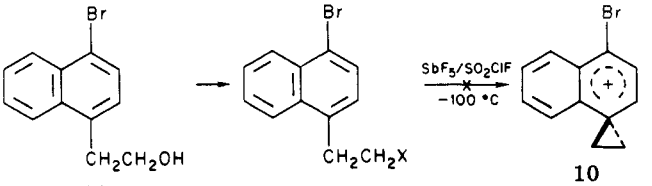
6 8

at -90 °C. The ^{13}C NMR spectrum showed nine peaks which are consistent with the formation of ion **6**. The most deshielded peak at $\delta_{^{13}C}$ 166.5 is assigned to C_{10}. Another low-field peak at $\delta_{^{13}C}$ 157.0 is assigned to C_{11}, C_{14}. The proton-coupled spectrum enabled assignments of C_2, C_7 at $\delta_{^{13}C}$ 142.6, C_4, C_5 at $\delta_{^{13}C}$ 136.6, C_{12}, C_{13} at $\delta_{^{13}C}$ 133.1, C_3, C_6 at $\delta_{^{13}C}$ 130.0, and C_1, C_8 at $\delta_{^{13}C}$ 122.5. Similarly the two aliphatic region peaks at $\delta_{^{13}C}$ 40.8 and 45.9 are assigned to spirocarbon C_9 and symmetrical cyclopropane methylenes C_{15}, C_{16}, respectively. Upon warming the solution of ion **6** up to -60 °C, it cleanly rearranged to benzylic ion **8** by ready opening of the cyclopropane ring followed by a 1,2 hydride shift. The ^{13}C spectrum of ion **8** gave 16 absorptions, which is in accord with the frozen-out structure of ion **8**. The low-field absorptions at $\delta_{^{13}C}$ 180.4 and 166.8 are assigned to C_{10} and C_{15}. The proton-coupled spectrum enabled tentative assignments of C_{11}, C_{14}, C_9, C_{12}, C_{13} at $\delta_{^{13}C}$ 144.7, 139.3, 135.0, 133.9, 133.1 and C_2, C_7, C_4, C_5, C_3, C_6, C_1, C_8 at $\delta_{^{13}C}$ 142.5, 141.9, 136.9, 135.5, 131.6, 131.2, 129.4, 124.3. The C_{16} methyl is assigned at $\delta_{^{13}C}$ 22.0. Structure of ion **8** was further proved by preparing it independently from 9-(α-hydroxyethyl)-10-bromoanthracene (**9**).

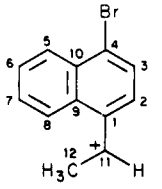


9 8

Attempted Preparation of 4-Bromo-α-ethylenenaphthalenium Ion (10). Ionization of 1-(2-chloroethyl)-4-bromonaphthalene (**11a**)[12] or 1-(2-fluoroethyl)-4-bromonahthphalene (**11b**)[13] in SbF_5/SO_2ClF solution at -110 °C did not give ion **10**, instead we observed only the rearranged benzylic ion **12**. This means that either the



11 11a, X = Cl 11b, X = F 10



12

ion **10** is not formed or more probably it is unstable and rearranges to ion **12** at -110 °C. The ^{13}C NMR spectrum of ion **12** showed 12 peaks which were consistent for the unsymmetrical structure **12**. The most deshielded peak at $\delta_{^{13}C}$ 200.0 is assigned to C_{11}. The proton-coupled spectrum enabled assignments of C_4, C_9, C_1, and C_{10} at $\delta_{^{13}C}$ 173.1, 137.6, 136.6, 134.8 and C_2, C_7, C_5, C_6, C_3, C_8 at $\delta_{^{13}C}$ 148.8, 140.3, 137.6, 133.5, 132.8, 124.0. The peak at $\delta_{^{13}C}$ 24.1 is assigned to the C_{12} methyl group. The structure of ion **12** is further proved by preparing it independently from 1-(4-bromo-α-naphthyl)ethyl alcohol (**13**)[14] and comparing the identical ^{13}C NMR spectra.

(9) Alcohol **7a** was prepared by known procedure; Mikhailov, B. M. *Izv. Akad. Nauk SSSR Ser. Khim.* **1948**, 420; *Chem. Abstr.* **1937**, *43*, 209c.

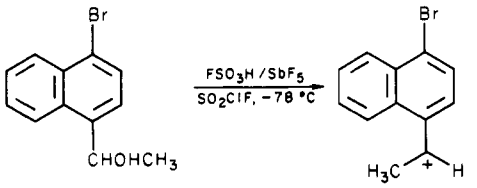
(10) Fluoride **7** was prepared from alcohol **7a** by Middleton's procedure; Middleton, W. J. *J. Org. Chem.* **1975**, *40*, 574 (see Experimental Section).

(11) Benzylic alcohol **9** was prepared from 9,10-dibromoanthracene, *n*-butyllithium, and acetaldehyde (see Experimental Section).

(12) Chloride **11a** was prepared from alcohol **11** by thionyl chloride/pyridine reaction.

(13) Fluoride **11b** was obtained from alcohol **11** by using Middleton's method.[10]

(14) Tsuno, Y.; Sawada, M.; Fujii, T.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3347.



13 12

Conclusions

Obtaining ions **2a–c** and **6** upon ionization of precursors **1a–c** and **7** under stable ion conditions clearly indicates aryl participation of the 4-halophenyl as well as of the 10-bromoanthryl group. In ions **2a–c** the deshielding effect of the C_4 chemical shift increases as the electronegativity of halogen atoms decreases, indicating that n–π back donation is greater in fluoro than in chloro and bromo carbocations. Also the more electronegative the halogen atom, the more stable the carbocation formed. The present study thus extends our knowledge of "phenonium ions" to ring-halogenated systems.

Experimental Section

All the melting and boiling points are uncorrected. All the ^{13}C NMR spectra were recorded on a Varian FT-80 spectrometer equipped with a broad-band probe and a variable-temperature control. Proton NMR spectra were recorded on a Varian A-56/60A spectrometer. All the chlorides **1a–c** were prepared by thionyl chloride/pyridine reaction with the corresponding alcohols obtained from Aldrich Chemical Co., and their data are compared with literature.[6] Alcohol **4** was prepared by methyllithium reaction with *p*-bromobenzaldehyde, bp 126–128 °C (10 mm) (lit.[7] bp 128 °C (10 mm). 9-(2-Hydroxyethyl)-10-bromoanthracene (**7a**) was prepared by literature procedure.[9] Alcohol **13** was easily prepared from 1,4-dibromonaphthalene, *n*-butyllithium, and acetaldehyde reaction, mp 71–72 °C (lit.[14] mp 70–72 °C). All the new compounds **7**, **9**, **11**, **11a,b** gave satisfactory elemental analyses.

9-(β-Fluoroethyl)-10-bromoanthracene (7). Alcohol **7a** (10 mmol) was dissolved into 30 mL of methylene chloride at –78 °C under an inert atmosphere and (diethylamino)sulfur trifluoride (12 mmol) in 10 mL of methylene chloride was added dropwise. The reaction mixture was warmed up to room temperature and stirred overnight. Thereafter it was poured into cold water and extracted with methylene chloride. The organic layer washed with water, $NaHCO_3$ solution, and finally with brine solution. Drying and evaporation of solvent gave yellowish solid which was recrystallized with hexane–chloroform to give **7**, yield 90%; mp 126–127 °C; ^{13}C NMR ($CDCl_3$) $\delta_{^{13}C}$ 131.2, 130.4, 128.9, 126.9, 126.4, 126.0, 124.3, 123.4, 83.0 (d, J_{C-F} = 172.3 Hz), 29.1 (d, J_{C-F} = 21.4 Hz).

9-(α-Hydroxyethyl)-10-bromoanthracene (9). To a solution of 9,10-dibromoanthracene (10 mmol) in 50 mL of dry THF at –78 °C was added 12 mmol of *n*-butyllithium, and the reaction mixture was stirred at this temperature for additional 1 h. Acetaldehyde (10 mmol) in 10 mL of dry THF was added dropwise, and the reaction mixture was warmed up to room temperature and stirred an additional 1 h. Usual workup and recrystallization of the solid residue by chloroform–hexane gave **9** in 85% yield: mp 180–182 °C dec; ^{13}C NMR ($CDCl_3$) $\delta_{^{13}C}$ 23.0, 71.2, 122.9, 123.1, 124.9, 125.0, 125.3, 124.7, 126.1, 126.4, 127.0, 128.9, 131.0, 134.5.

1-(2-Hydroxyethyl)-4-bromonaphthalene (11). Alcohol **11** was conveniently prepared from 1,4-dibromonaphthalene, *n*-butyllithium, and ethylene oxide in 70% yield; bp 160–162 °C (0.4 mm), and analyzed by its ^{13}C NMR spectrum. ^{13}C NMR ($CDCl_3$) $\delta_{^{13}C}$ 138.3, 133.4, 127.8, 127.0, 126.7, 125.8, 125.5, 124.4, 123.6, 62.7, 36.1.

1-(2-Chloroethyl)-4-bromonaphthalene (11a). Chloride **11a** was prepared from alcohol **11** in the usual way by using thionyl chloride and pyridine in refluxed ether: yield 70%; bp 150–152 °C (0.4 mm); ^{13}C NMR ($CDCl_3$) δ 133.9, 132.0, 129.4, 128.0, 127.4, 127.0, 127.0, 126.2, 125.6, 123.5, 43.7, 36.0.

1-(2-Fluoroethyl)-4-bromonaphthalene (11b). Fluoride **11b** was conveniently prepared from alcohol **11** by using Middleton's procedure:[10] yield 87%; bp 130–132 °C (0.4 mm); ^{13}C NMR ($CDCl_3$) $\delta_{^{13}C}$ 132.5, 130.0, 129.3, 128.5, 127.8, 127.5, 126.6, 126.0, 124.3, 122.5, 83.5 (d, J_{C-F} = 170.4 Hz), 34.0 (d, J_{C-F} = 21.1 Hz).

General Procedure for Preparing the α-Ethylenehaloarenium Ions. In a carbon-13 NMR tube superacid (0.5 mL) is dissolved into 1–1.5 mL of SO_2ClF generally at –78 °C (or the temperatures indicated) with continuous stirring. The solid or liquid substrate to be ionized was added in portions to the cold acid solution in the tube while stirred on a Vortex mixer till a homogeneous ion solution was obtained.

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

Registry No. **1a**, 332-43-4; **1b**, 32327-70-1; **1c**, 23386-17-6; **2a**, 90867-08-6; **2b**, 90867-09-7; **2c**, 90885-95-3; **3c**, 67595-65-7; **4**, 5391-88-8; **6**, 90867-07-5; **7**, 90867-01-9; **7a**, 90867-06-4; **8**, 90867-04-2; **9**, 90867-02-0; **10**, 90867-10-0; **11**, 90867-05-3; **11a**, 58149-81-8; **11b**, 90867-03-1; **12**, 90885-91-9; **13**, 58149-70-5; *p*-BrC_6H_4CHO, 1122-91-4; CH_3CHO, 75-07-0; 9,10-dibromoanthracene, 523-27-3; ethylene oxide, 75-21-8; 1,4-dibromonaphthalene, 83-53-4.

Medium-Ring Systems. 5.[1] Synthesis and Base-Catalyzed Isomerizations of Medium-Ring Cycloalkenones with Electron-Withdrawing Substituents[2]

Ronnie C. Mease and Jerry A. Hirsch*

Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079

Received February 17, 1984

Medium-ring 3-cycloalkenones with electron-withdrawing substituents at the 3-position have been synthesized and subjected to base-catalyzed isomerizations. In a given ring size in the seven- and eight-membered carbocycles, the substituents studied caused similar shifts in the equilibria toward the 3-cycloalkenones relative to the unsubstituted cases. Steric effects of the substituents are therefore not significant. As the ring size is increased, the preference for the 3-cycloalkenone becomes more pronounced. In the nine- and ten-membered systems, an additional equilibrium involving formation of 4-cycloalkenones appears. Decreased effectiveness of conjugative interactions in endocyclic dienolates and in 2-cycloalkenones with increasing ring size is suggested.

The ability of a substituent to stabilize or destabilize a double bond has been quantitatively evaluated by Hine's[3] "double-bond stabilization parameters". In this approach, an equilibrium is established where the given substituent

0022-3263/84/1949-2925$01.50/0