C with rapid vortex mixing. The "magic acid", SbF_5/FSO_3H (1:1 molar ratio) concentration in the solution was 3 M. The concentration of the ion based on the alcohol added was ~0.5 M. Transfer of the solutions under nitrogen to an 8-mm NMR tube was achieved via a cooled double-ended syringe, as described previously.[15]

Registry No. 3 (Z = 4-OCH_3), 35144-43-5; **3** (Z = 4-CH_3), 14290-14-3; **3** (Z = 4-F), 51804-44-5; **3** (Z = 4-Cl), 76499-76-8; **3** (Z = 3-CH_3), 76499-77-9; **3** (Z = H), 14290-13-2; **3** (Z = 3-F), 76499-78-0; **3** (Z = 3-Cl), 76499-79-1; **3** (Z = 3-CF_3), 76499-80-4; **3** (Z = 3,5-Cl_2), 76499-81-5; **3** (Z = 4-CF_3), 36043-26-2; **3** (Z = 3,5-$(CF_3)_2$), 76499-82-6; **4** (Z = 4-OCH_3), 76499-83-7; **4** (Z = 4-CH_3), 76499-84-8; **4** (Z = 4-F), 76499-85-9; **4** (Z = 4-Cl), 76499-86-0; **4** (Z = 3-CH_3), 76499-87-1; **4** (Z = H), 76499-88-2; **4** (Z = 3-F), 76499-89-3; **4** (Z = 3-Cl), 76499-90-6; **4** (Z = 3-CF_3), 76499-91-7; **4** (Z = 3,5-Cl_2), 76499-92-8; **4** (Z = *P*-CF_3), 76499-93-9; **5** (Z = 4-OCH_3), 30068-21-4; **5** (Z = 4-CH_3), 5398-04-9; **5** (Z = 4-F), 7119-12-2; **5** (Z = 4-Cl), 3947-53-3; **5** (Z = 3-CH_3), 76499-94-0; **5** (Z = 3-F), 76529-20-9; **5** (Z = 3-Cl), 58977-34-7; **5** (Z = 3-CF_3), 10015-15-3; **5** (Z = 3,5-Cl_2), 76499-95-1; **5** (Z = *P*-CF_3), 10015-16-4; **5** (Z = 3,5-$(CF_3)_2$), 76499-96-2; **6** (Z = 4-CH_3), 76499-97-3; **6** (Z = 4-F), 76499-98-4; **6** (Z = 4-Cl), 76499-99-5; **6** (Z = 3-CH_3), 76500-00-0; **6** (Z = H), 4436-96-8; **6** (Z = 3-F), 76500-01-1; **6** (Z = 3-Cl), 76500-02-2; **6** (Z = 3-CF_3), 76500-03-3; **6** (Z = 3,5-Cl_2), 76500-04-4; **6** (Z = *p*-CF_3), 76500-05-5; **6** (Z = 3,5-$(CF_3)_2$), 76500-06-6; 4-*p*-anisyl-3-heptene, 6465-99-2.

Carbon-13 Nuclear Magnetic Resonance Studies of Carbocations. 5.[1] Effect of Increasing Electron Demand on the Carbon-13 Chemical Shifts of 3-Aryl-3-pentyl and 2-Aryl-2-adamantyl Carbocations. Correlation of $\Delta\delta^{C^+}$ with Enhanced Substituent Constants σ^{C^+}

David P. Kelly,* Margot J. Jenkins, and Robert A. Mantello

Department of Organic Chemistry, University of Melbourne, Parkville, Victoria, Australia 3052

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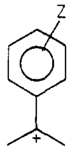
The ^{13}C chemical shifts for a range of meta- and para-substituted 3-phenyl-3-pentyl and 2-phenyl-2-adamantyl carbocations have been measured in $FSO_3H/SbF_5/SO_2ClF$ solutions. The cationic carbon substituent chemical shifts ($\Delta\delta^{C^+}$) show only a fair correlation with σ^+ constants, but when plotted against the new σ^{C^+} constants, excellent linear correlations are obtained. The 3-aryl-3-pentyl system gives a correlation coefficient of $r = 0.999$ with a slope of $\rho^{C^+} = -17.17$, and the 2-aryl-2-adamantyl system gives $r = 0.998$ with $\rho^{C^+} = -16.08$. These nearly perfect linear correlations, together with that realized previously for 1-aryl-1-cyclopentyl cations, confirm the validity and usefulness of the enhanced substituent constants.

The correlation of ^{13}C chemical shifts with Hammett–Brown σ^+ constants has received considerable attention over the past few years.[2-4] On the assumption (i) of a late transition state for the solvolysis of cumyl chlorides in acetone[5] and (ii) that ^{13}C chemical shifts were linearly proportional to charge density, it was not unreasonable to expect the σ^+ constants to correlate ^{13}C shifts of the fully formed carbocations in superacids. Thus Olah and coworkers noted an approximate linearity in the plot of cationic carbon shifts (δ^{C^+}) against σ^+ for a series of substituted *tert*-cumyl cations.[3] However, reinvestigation of these cations showed that the correlation was only fair ($r = 0.967$) and that the line of best fit failed to pass through the point for the parent *tert*-cumyl cation (**1**, Z = *p*-H).[4] We suggested that the problem was due to our failure to allow for the extra electron demand in these fully formed cations compared to that for the solvolytic transition states. That is, there is enhanced charge delocalization in the cations containing electron-donating substituents. Consequently, we proposed a new set of "super sigma" values, σ^{++}, for correlation of cationic carbon shifts which were derived by extrapolating the line of best fit for electron-withdrawing substituents through the origin (i.e., for δ^{C^+} of **1** (Z = *p*-H), $\sigma^+ = 0$).

As the data in the earlier studies were relatively few, we have recently obtained the ^{13}C spectra of an extended range of both meta- and para-substituted *tert*-cumyl cations.[1] When plotted against σ^+_m, the cationic carbon substituent chemical shifts ($\Delta\delta^{C^+}$)[6] for the meta cations give a good correlation ($r = 0.990$, $\sigma^+ = -18.18$). Using the original approach of Brown and Okamoto,[7] we therefore used the slope of the line (−18.18) for the meta substituents to calculate new constants, values of which would place the $\Delta\delta^{C^+}$ values for the para derivatives on the line. Thus a modified Hammett–Brown constant was derived (eq 1),

$$\Delta\delta^{C^+} = \rho^{C^+}\sigma^{C^+} \tag{1}$$

where σ^{C^+} is the enhanced substituent constant having the following values: −2.02, *p*-OCH_3; −0.67, *p*-CH_3; −0.40, *p*-F; −0.24, *p*-Cl; −0.19, *p*-Br; 0.79, *p*-CF_3; 0.13, *m*-CH_3; −0.14, *m*-$CH(CH_3)_2$; 0.35, *m*-F; 0.36, *m*-Cl; 0.33, *m*-Br; 0.56, *m*-CF_3; 0.66, 3,5-Cl_2; 1.03, 3,5-$(CF_3)_2$. When applied to the data for the 1-aryl-1-cyclopentyl cations **2**, the σ^{C^+} constants give an excellent correlation: $r = 0.999$, $\sigma^{C^+} = -16.84$.



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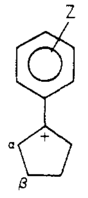

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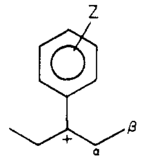

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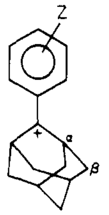

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We now report similar excellent correlations for the plots against $\Delta\delta^{C^+}$ for two different systems, the 3-aryl-3-pentyl (**3**) and the multicyclic 2-aryl-2-adamantyl (**4**) cations.

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(1) For Part 4, see: Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad.* Sci. *U.S.A.* **1980**, *77*, 6956.

(2) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1977**, *30*, 1993 and references therein.

(3) Olah, G. A.; Porter, R. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044.

(4) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1978**, *31*, 1209.

(5) Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.

(6) In order to reproduce the form of the Hammett–Brown plot, we define $\Delta\delta^{C^+} = [\delta^{C^+}(R = H) - \delta^{C^+}(R \neq H)]$ ppm (see ref 1).

(7) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

Table I. ^{13}C Chemical Shifts of 3-Aryl-3-pentyl Carbocations 3 in $FSO_3H/SbF_5/SO_2ClF$ at −70 °C

	chemical shift[a]									
substituent	C^+	C_α	C_β	Z	C_1	C_2	C_3	C_4	C_5	C_6
4-OCH_3	227.9	33.8	17.0	59.9	132.6	145.8	120.6	182.9	120.6	145.8
4-CH_3	251.6	36.9	18.4	25.3	136.9	142.2	134.8	175.4	134.8	142.2
4-F	255.8	38.0	18.6		135.8	147.5 (16)	122.1 (21)	180.9 (295)	122.1 (21)	147.5 (16)
4-Cl	259.0	38.4	18.8		136.9	142.8	134.3	166.1	134.3	142.8
3-CH_3	260.9	38.2	19.0	20.6	138.9	140.1[b]	144.9	157.6	133.4	141.8[b]
H	263.4	38.7	19.0		138.9	142.6	133.8	156.9	133.8	142.6
3-F	269.0	40.2	19.6/ 19.2[c]		140.1 (8)	125.6 (21)	164.7 (254)	142.6 (21)	135.3 (8)	139.0
3-Cl	269.2	40.0	19.6/ 18.9[c]		141.9	140.9[b]	134.6	154.5	139.6[b]	140.0[b]
3-CF_3	272.4	40.8	19.1	123.3 (272)	138.3	137.1	135.4 (35)	150.1	134.4	144.7
3,5-Cl_2[d]	274.4	41.5	19.6		138.5	140.9	139.8	152.1	139.8	140.9
4-CF_3[d]	275.7	41.6	19.6	122.9 (273)	139.9	142.0	129.8	150.5 (34)	129.8	142.0

[a] ±0.1 ppm from external Me_4Si. ^{13}C–^{19}F coupling constants (hertz) in parentheses. [b] Assignments may be interchanged. [c] Nonequivalent. [d] Prepared from the alkene and measured at −80 °C.

Table II. ^{13}C Chemical Shifts of 2-Aryl-2-adamantyl Carbocations 4 in $FSO_3H/SbF_5/SO_2ClF$ at −70 °C

	chemical shift[a]											
substituent	C^+	C_α	C_β	C_γ	C_δ	Z	C_1	C_2	C_3	C_4	C_5	C_6
4-OCH_3[b]	237.5	44.3	45.6	28.7	36.4	59.2	130.1	143.0	120.2	182.7	120.2	143.0
4-CH_3	260.4	49.0	48.1	29.6	36.6	24.6	135.1	138.8	134.3	173.0	134.3	138.8
4-F	265.2	50.8	49.0	29.8	36.9		134.4	143.6 (16)	121.7 (22)	181.0 (289)	121.6 (22)	143.6 (16)
4-Cl	268.2	51.5	49.7	30.0	36.7		135.6	139.3	133.9	164.1	133.9	139.3
3-CH_3	269.8	51.5	49.4	29.8	36.6	20.7	138.9	136.2[c]	145.1	155.8	133.1	137.6[c]
H	271.6	51.5	49.5	29.8	36.5		137.4	138.3	133.1	154.4	133.1	138.3
3-F	277.0	54.5	51.2	30.3	36.7		138.8	122.5 (22)	165.3 (254)	140.2 (22)	135.2	135.2
3-Cl	277.2	54.2	51.6	30.2	36.7		138.8[c]	134.3	139.6[c]	152.4	136.8[c]	136.0[c]
3-CF_3	280.1	55.2	51.9	30.5	36.9	123.5 (273)	137.5	134.0	134.9 (35)	148.0	134.0	140.7
3,5-Cl_2	281.8	56.5	52.8	30.5	36.9		139.2	134.4	140.0	149.9	140.0	134.4
4-CF_3	283.3	56.4	52.9	30.5	36.9	*d*	139.8	137.9	129.5	149.3 (35)	129.5	137.9
3,5-$(CF_3)_2$[e]	286.2	58.7	54.3	31.1	37.1	122.9 (273)	137.9	135.7	136.0 (37)	142.5	136.0 (37)	135.7

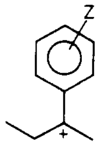
[a] ±0.1 ppm from external $(CH_3)_4Si$. ^{13}C–^{19}F coupling constants (hertz) in parentheses. [b] The chemical shifts of this cation vary considerably with conditions. These data are for 0.48 M cation in 1:1 FSO_3H–SbF_5 in SO_2ClF at −40 °C. Other values we recorded for 0.33 M cation in 6:1 FSO_3H–SbF_5 in SO_2ClF at −80 °C were (in order as above) 241.6, 45.8, 45.8, 29.1, 36.4, 60.6, 130.8, 142.8, 119.8, 181.0, 119.8, and 142.8 ppm. D. G. Farnum has observed a variation in the cationic carbon shift from 237.9 to 280.4 ppm with different acid concentrations (personal communication). [c] Assignments may be interchanged. [d] Signals too weak to measure. [e] From the chloride.

Results and Discussion

The precursor alcohols, 3-aryl-3-pentanols and 2-aryl-2-adamantanols, were prepared by standard Grignard reactions of 3-pentanone and 2-adamantanone with the appropriate bromobenzenes. Ionization of these alcohols in 1:1 FSO_3H-SbF_5 in SO_2ClF solutions at −78 °C generally yielded dark red-brown solutions, the ^{13}C spectra of which were recorded at −70 °C. In some cases the resulting solutions were dark green, e.g., 4-3,5-Cl_2 and 4-*p*-OCH_3, but gave satisfactory spectra with no species other than the cation present.

2-[3,5-Bis(trifluoromethyl)phenyl]-2-adamantanol did not ionize cleanly in either 1:1 FSO_3H-SbF_5 or FSO_3H. However the ion was generated cleanly from the corresponding chloride in FSO_3H–SbF_5. Similarly, (3,5-dichlorophenyl)-, *p*-(trifluoromethyl)phenyl-, and 3-[3,5-bis(trifluoromethyl)phenyl]-3-pentanol did not ionize cleanly. Attempted chlorination of these alcohols yielded the corresponding olefins which were then used to prepare the cations. Protonation of two of these olefins in 1:1 FSO_3H–SbF_5 in SO_2ClF solutions at −78 °C yielded the corresponding cations 3-3,5-Cl_2 and 3-*p*-CF_3. However, all attempts to generate 3-3,5-$(CF_3)_2$ in different super acids, at different temperatures, and from different precursors were unsuccessful.

The chemical shifts of the cations 3 and 4 are given in Tables I and II. When plotted against σ^+ constants, the cationic carbon substituent chemical shifts for 3 give only a fair correlation: $r = 0.954$, $\rho^+ = -28.71$. However, when plotted against the new, enhanced substituent constants σ^{C^+}, the $\Delta\delta^{C^+}$ values give an excellent correlation: $r = 0.999$, $\rho^{C^+} = -17.17$ (standard deviations: ρ^{C^+}, 0.15; $\Delta\delta^{C^+}$, 0.11). Similar excellent correlations are obtained for the related acyclic systems 5 ($r = 0.9998$, $\rho^{C^+} = -17.78$) and 6 ($r = 0.999$, $\rho^{C^+} = -14.57$) reported by Brown, Periasamy, and Liu.[8]



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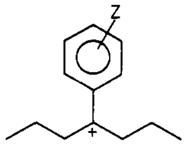

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Table III. Physical Constants for Substituted-3-phenyl-3-pentanols (7) and 2-Phenyl-2-adamantanols (8)

	7		
substituent	bp, °C (mm)	η_{D}^{20}	8, mp,[a] °C
4-OCH_3	68–70 (0.05)[b]	1.5230	101–102
4-CH_3	58–61 (0.1)[c]	1.5124	73–75[d]
4-F	49–52 (0.1)	1.4958	80–81
4-Cl	64–67 (0.1)	1.5232	103–105[e]
3-CH_3	53–55 (0.1)	1.5129	49–53
H	52–54 (0.1)[f]	1.5145	78–80[g]
3-F	42–43 (0.03)	1.4941	82–84
3-Cl	62–64 (0.05), 33–37[h]		85–87
3-CF_3	39–42 (0.05)	1.4638	81–83
3,5-Cl_2	61–62[h]		101–103
4-CF_3	41–43 (0.05)	1.4635	73.5–75.5
3,5-$(CF_3)_2$	56–58 (0.1)	1.4301	90–91

[a] Sealed capillary. [b] Lit. bp 87 °C (0.01 mm), η_{D}^{25} 1.5278: Dutton, G. G. S.; Hillman, M. E. D.; Moffatt, J. G. *Can. J. Chem.* **1964**, *42*, 480. Lit. bp 100–110 °C (0.2 mm): König, W.; Geiger, R.; Siedel, W. *Chem. Ber.* **1968**, *101*, 681. [c] Lit. bp 87.5 °C (1.8 mm), η_{D}^{20} 1.5139; Liberman, A. L.; Tyan'kima, N. I. *Neftekhimiya* **1969**, *9*, 171. [d] Lit. mp 75–77 °C: Tanida, H.; Tsushima, T. *J. Am. Chem. Soc.* **1970**, *92*, 3397. [e] Lit. mp 105.5–107.5 °C; reference as in *d*. [f] Lit. bp 113–115 °C (16 mm), η_{D}^{20} 1.5167: Traynelis, V. J.; Hergenrother, W. L.; Livingston, J. R.; Valicenti, J. A. *J. Org. Chem.* **1962**, *27*, 2377. [g] Lit. mp 78.5–79 °C; reference as in *d*. [h] Melting point.

When plotted against σ^+ constants, $\Delta\delta^{C^+}$ values of the 2-adamantyl cations **4** also show only a fair correlation ($r = 0.943$, $\rho^+ = -24.76$), but when they are plotted against σ^{C^+}, an excellent correlation is obtained with $r = 0.998$ and $\rho^{C^+} = -16.08$ (standard deviations: ρ^{C^+}, 0.28; $\Delta\delta^{C^+}$, 0.22).

Inspection of Tables I and II shows that the α-carbon shifts also increase systematically with increasing electron demand. However, from plots (not shown) of the substituent chemical shifts ($\Delta\delta^{C_\alpha}$) against σ^+ and σ^{C^+} it is apparent that another substituent constant of intermediate value would be most appropriate.[9] This is best derived from the methyl carbon shifts of meta-substituted *tert*-cumyl cations in a manner similar to that for σ^{C^+}. Such a constant ($\sigma^{\alpha C^+}$) has now been derived[10] and gives excellent correlations with $\Delta\delta^{C_\alpha}$ for both **3** ($r = 0.998$, $\rho^{\alpha C^+} = -3.96$) and **4** ($r = 0.997$, $\rho^{\alpha C^+} = -6.23$).

The β-carbon shifts of **3** show a 1.4-ppm increase from p-OCH_3 to p-CH_3 and then another 1.2 ppm to p-CF_3. This trend is similar to that observed in **5** and in contrast to that in **6** where a change of 4.2 ppm is observed from p-OCH_3 to p-CF_3.[8] Deshielding of the β-carbons with increasing electron demand is even more pronounced in **4**, ranging from δ 45.6 for p-OCH_3 to δ 54.3 for 3,5-$(CF_3)_2$. Delocalization of charge into the alicyclic skeleton is well-known in 1-adamantyl systems and is attributed to overlap of the rear lobes of the tertiary carbons.[11] The marked dependence of the β-carbon shift on electron demand observed here indicates that delocalization can also occur at C_2, possibly by C–C hyperconjugation of the C_α–C_β bond with the vacant p orbital. We are examining this proposal with the aid of the known dependence of $^1J_{^{13}C_\alpha H}$ upon dihedral angle in carbocations.[12]

Conclusion

The excellence of the correlations of $\Delta\delta^{C^+}$ with σ^{C^+} constants in the series of cations **2–6** confirms the validity of the original proposal of using enhanced substituent constants to correlate carbon shifts in cations and the usefulness of the new σ^{C^+} constants. We are continuing to explore their utility in other systems.

Experimental Section

NMR Spectra. The ^{13}C NMR spectra were recorded at −70 °C on either a hybrid Varian–Digilab-PDP-15 spectrometer operating at 15.08 MHz in the FT mode or on a JEOL FX-100 spectrometer in 10-mm tubes containing a concentric 3-mm capillary of acetone-d_6 and $(CH_3)_4Si$ as a reference. Data were accumulated by using 8192 data points, spectral widths of 5000 or 8000 Hz (FX-100), and pulse angles of 60° or 45° (FX-100). Chemical shifts are reported ±0.1 ppm from external $(CH_3)_4Si$. Assignments were based on those reported previously for *tert*-cumyl,[4] cyclopentyl,[1] and adamantyl cations[11] and on the basis of off-resonance, proton-decoupled spectra and ^{13}C–^{19}F coupling constants. Where ambiguity arises in the assignment of the protonated aryl resonances, this has been indicated in the tables. In the case of **3**-m-CH_3 the assignment of C_5 as the lowest frequency aryl carbon is confirmed by the proton-coupled spectrum, the resonance at δ 133.1 appearing as a clean doublet ($^1J_{CH} = 170$ Hz) with no long-range coupling ($^3J_{CH}$).[13]

Precursors. The 3-aryl-3-pentanols (**7**) and 2-aryl-2-adamantanols (**8**) were prepared by standard Grignard procedures from 3-pentanone and 2-adamantanone with the corresponding bromobenzenes. All of these alcohols gave satisfactory ^1H and ^{13}C NMR spectra, and their physical constants are summarized in Table III. Satisfactory (≤0.3%) microanalytical data have been obtained for all new compounds.

2-[3,5-Bis(trifluoromethyl)phenyl]-2-chloroadamantane was prepared from the alcohol by treatment with thionyl chloride in pyridine at 60 °C for 7 h. Dilution with ether, washing with sodium bicarbonate, drying, and evaporation yielded the chloro compound: mp 115–117 °C (pentane); ^{13}C NMR ($CDCl_3$) δ 147.0 (C_1), 132.2 ($C_{3,5}$, $J = 33$ Hz), 125.5 ($C_{2,6}$), 123.3 (CF_3, $J = 272$ Hz), 121.3 (C_4), 76.4 (CCl), 37.8, 37.1, 34.7, 33.5, 27.0, 26.5. Attempted chlorination of 3-[4-(trifluoromethyl)phenyl]-, 3-(3,5-dichlorophenyl)-, and 3-[3,5-bis(trifluoromethyl)phenyl]-3-pentanols with thionyl chloride in pyridine resulted in the formation of the corresponding trisubstituted olefins, which were identified by their ^1H spectra. These olefins were used without further purification to generate the carbocations.

Carbocations. The cations **3** were prepared by careful addition of a solution of the precursor (ca. 200 mg) in SO_2ClF at −78 °C to a rapidly (vortex) stirred solution of 1:1 FSO_3H–SbF_5 in SO_2ClF. The resulting cation solutions were in the range 0.3–0.7 M. We were unable to prepare the 3-[3,5-bis(trifluoromethyl)phenyl]-3-pentyl cation in either FSO_3H–SbF_5 in SO_2ClF or FSO_3H/SO_2ClF from either the alcohol or the alkene at either −120 or −78 °C. The ^{13}C spectra generally showed either broad resonances or the presence of neutral aryl species. Such neutral species have been identified recently in the attempted preparation of 2-methyl-1-arylcycloalkyl cations.[14]

The cations **4** were prepared by slow addition of the powdered solid alcohol [chloride in the case of **4**-3,5-$(CF_3)_2$] to a rapidly (vortex) stirred solution of 1:1 FSO_3H–SbF_5 in SO_2ClF at −78 °C. Transfer of the resulting dark colored solutions to the NMR tubes was achieved via a double-ended syringe needle.[15] The con-

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(8) Brown, H. C.; Periasamy, M.; Liu, K-T. *J. Org. Chem.*, preceding paper in this issue.

(9) For **3**: $\Delta\delta^{C_\alpha}$ vs. σ^+, $r = 0.985$, $\rho^+ = -4.96$; σ^{C^+}, $r = 0.987$, $\rho^{C^+} = -2.83$. For **4**: $\Delta\delta^{C_\alpha}$ vs. σ^+, $r = 0.989$, $\rho^+ = -7.65$; σ^{C^+}, $r = 0.984$, $\rho^{C^+} = -4.67$.

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centrations of these solutions were in the range 0.3–0.5 M. Apart from 4-*p*-OCH$_3$, the cations did not exhibit significant variations in chemical shifts with changes of temperature, superacids, or concentrations. In the case of 4-*p*-OCH$_3$ the variation may be due to equilibration with an O-protonated or Lewis acid associated species.

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Registry No. **3** (Z = 4-OCH$_3$), 76481-14-6; **3** (Z = 4-CH$_3$), 76481-15-7; **3** (Z = 4-F), 51804-43-4; **3** (Z = 4-Cl), 76481-16-8; **3** (Z = 3-CH$_3$), 76481-17-9; **3** (Z = H), 76481-18-0; **3** (Z = 3-F), 76481-19-1; **3** (Z = 3-Cl), 76481-20-4; **3** (Z = 3-CF$_3$), 76481-21-5; **3** (Z = 3,5-Cl$_2$), 76481-22-6; **3** (Z = 4-CF$_3$), 76481-23-7; **4** (Z = 4-OCH$_3$), 76481-24-8; **4** (Z = 4-CH$_3$), 76481-25-9; **4** (Z = 4-F), 51804-53-6; **4** (Z = 4-Cl), 76481-26-0; **4** (Z = 3-CH$_3$), 76481-27-1; **4** (Z = H), 52873-73-1; **4** (Z = 3-F), 76481-28-2; **4** (Z = 3-Cl), 76481-29-3; **4** (Z = 3-CF$_3$), 76481-30-6; **4** (Z = 3,5-Cl$_2$), 76481-31-7; **4** (Z = 4-CF$_3$), 76481-32-8; **4** (Z = 3,5-(CF$_3$)$_2$), 76481-33-9; **7** (Z = 4-OCH$_3$), 17138-75-9; **7** (Z = 4-CH$_3$), 22975-57-1; **7** (Z = 4-F), 76481-34-0; **7** (Z = 4-Cl), 76481-35-1; **7** (Z = 3-CH$_3$), 76481-36-2; **7** (Z = H), 1565-71-5; **7** (Z = 3-F), 76481-37-3; **7** (Z = 3-Cl), 76481-38-4; **7** (Z = 3-CF$_3$), 76481-39-5; **7** (Z = 3,5-Cl$_2$), 76481-40-8; **7** (Z = 4-CF$_3$), 76481-41-9; **7** (Z = 3,5-(CF$_3$)$_2$), 76481-42-0; **8** (Z = 4-OCH$_3$), 76481-43-1; **8** (Z = 4-CH$_3$), 29480-17-9; **8** (Z = 4-F), 76481-44-2; **8** (Z = 4-Cl), 29480-19-1; **8** (Z = 3-CH$_3$), 76481-45-3; **8** (Z = H), 29480-18-0; **8** (Z = 3-F), 76481-46-4; **8** (Z = 3-Cl), 76481-47-5; **8** (Z = 3-CF$_3$), 76481-48-6; **8** (Z = 3,5-Cl$_2$), 76481-49-7; **8** (Z = 4-CF$_3$), 76481-50-0; **8** (Z = 3,5-(CF$_3$)$_2$), 76481-51-1; 3-[4-(trifluoromethyl)phenyl]-2-pentene, 76481-52-2; 3-(3,5-dichlorophenyl)-2-pentene, 76481-53-3; 2-[3,5-bis(trifluoromethyl)phenyl]-2-chloroadamantane, 76498-69-6.

Stevens-Type Rearrangement of Open-Chain Analogues of Reissert Compounds. Evidence for Participation by Radical Intermediates

Andrew P. Stamegna and William E. McEwen*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

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The thermal rearrangements of the conjugate bases (**2**) of *N*-benzyl open-chain analogues of Reissert compounds give products formally derived from two competing [1,2] rearrangement–elimination reactions. The products of the major sequences of reactions are deoxybenzoins and benzonitriles, while those of the minor sequence are α-benzamidostilbenes. The results are compatible with a radical pair mechanism involving initial homolysis of the conjugate base **2** followed by two possible modes of radical recombination (Schemes I and II).

Table I. Rearrangement Reactions

Reissert analogue	Ar$_1$	Ar$_2$	Ar$_3$	% yield of 3
1a	C$_6$H$_5$	C$_6$H$_5$	C$_6$H$_5$	57
b	*p*-ClC$_6$H$_4$	C$_6$H$_5$	C$_6$H$_5$	94
c	*p*-CH$_3$OC$_6$H$_4$	C$_6$H$_5$	C$_6$H$_5$	100
d	2-furyl	C$_6$H$_5$	C$_6$H$_5$	63
e	3,4-(methylenedioxy)phenyl	C$_6$H$_5$	C$_6$H$_5$	55
f	C$_6$H$_5$	C$_6$H$_5$	*p*-ClC$_6$H$_4$	50
g	*p*-ClC$_6$H$_4$	C$_6$H$_5$	*p*-ClC$_6$H$_4$	87
h	*p*-CH$_3$OC$_6$H$_4$	C$_6$H$_5$	*p*-ClC$_6$H$_4$	96
i	C$_6$H$_5$	*p*-CH$_3$C$_6$H$_4$	C$_6$H$_5$	62
j	*p*-CH$_3$OC$_6$H$_4$	*p*-CH$_3$C$_6$H$_4$	C$_6$H$_5$	64

Although base-catalyzed rearrangements of Reissert compounds derived from quinoline and isoquinoline have been observed,[1,2] there have been no reports of analogous rearrangements for open-chain Reissert analogues other than a brief mention of this in our recent paper covering synthetic uses of such compounds.[3] We report here examples of several base-catalyzed rearrangement reactions of open-chain analogues of Reissert compounds and present evidence in support of a mechanism involving initial homolysis of each conjugate base, with two subsequent modes of radical pair recombination.

Open-chain analogues of Reissert compounds **1a–j** have been prepared by known methods.[3,4] The anions **2a–j** of these Reissert analogues have been generated by treatment of **1a–j** with sodium hydride in tetrahydrofuran solution,[4] and these anions, in turn, have been found to undergo rearrangement and fragmentation to the deoxybenzoins **3a–j** (eq 1). The results of the ketone preparations are summarized in Table I. This rearrangement is of interest, not only from a synthetic viewpoint but also from a mechanistic one, in that it bears striking similarities to the Stevens and related rearrangements.[5,6]

Since the participation of radical intermediates in the Stevens and related rearrangements is well documented,[6,8-19] it was decided to investigate the possible partici-

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