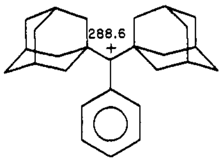
These authors observed that 1,1′-diadamantylphenylmethyl cation (**11**) exhibits a ^{13}C NMR shift at the carbonium carbon that is considerably downfield from the shift in the *tert*-cumyl cation (**12**).



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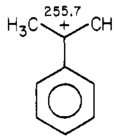

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However, the *tert*-cumyl system is clearly capable of overcoming the steric barrier to coplanarity in the fully developed ions.[14] The steric barrier in 1,1-diarylethyl cations (**1**), 2-aryl-2-norbornyl cations (**2**), and 3-aryl-3-nortricyclyl cations (**3**) should be correspondingly small. Consequently, it does not appear that such barriers can be responsible for the observed deviations in the ^{13}C plots for electron-withdrawing substituents. This conclusion has been tested further in the accompanying publication.[15]

We have considered four possible origins for the observed deviations in the $\Delta\delta C^+/\delta^{C^+}$ plots for certain benzylic systems containing strongly electron-withdrawing substituents: (1) steric inhibition to coplanarity,[8,9] (2) rapid equilibration (tert $\rightleftharpoons$ sec),[16] (3) enhanced electron supply from certain moieties,[7] and (4) inductive π polarization, as suggested by Brownlee and co-workers.[17] The studies reported in this and the accompanying publication[15] appear to rule out the steric origin. We are now testing the other explanations experimentally.

Experimental Section

Precursors. The 4′- or 5′-substituted *o*-methylphenyl-2-propyl alcohols **5** were synthesized by the reaction of acetone with the Grignard reagent prepared from the corresponding bromotoluenes **6**. All of these bromotoluenes **6** are commercially available except the 4′-OCH$_3$ and 5′-CF$_3$ derivatives. The 4′-OCH$_3$ (**6**) derivative was prepared by bromination of *m*-cresylmethyl ether with *N*-bromosuccinimide following a literature procedure.[18] The 5′-CF$_3$ (**6**) derivative was synthesized by bromination of *p*-(trifluoromethyl)toluene with bromine following a literature method.[19] The alcohol **5** derivatives Z = 4′-OCH$_3$ (mp 68 °C) and Z = H [bp 108 °C (20 mm)] have been reported previously from our laboratories.[10,20] The boiling point data for other derivatives are as follows: Z = 4′-CH$_3$, 117 °C (20 mm); Z = 4′-F, 56 °C (0.1 mm); Z = 5′-F, 59 °C (0.1 mm); and Z = 5′-CF$_3$, 67 °C (0.1 mm). All of these compounds gave ^{13}C NMR data in accordance with their structures. Satisfactory analytical data (<±0.3% for C, H, and F) were obtained for all of the new compounds.

Carbocations. The cations **4** were prepared by slow addition of the appropriate precursor as a solution in SO$_2$ClF at −78 °C to a solution of FSO$_3$H/SbF$_5$(1:1 M)/SO$_2$ClF cooled to −78 °C with rapid vortex mixing. The acid concentration in the solution was 3 M. The concentration of the ion based on the precursor 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.[21]

NMR Spectra. ^{13}C NMR spectra were recorded at −80 °C on a Varian CFT-20 spectrometer with 8-mm tubes containing a concentric 3-mm (o.d.) capillary tube of acetone-d_6 and Me$_4$Si, 8192 data points, a spectral width of 6000 Hz, and a pulse angle of 45°. Chemical shifts are in parts per millon downfield from external Me$_4$Si.

Registry No. **4** (Z = 4′-OCH$_3$), 83208-01-9; **4** (Z = 4′-CH$_3$), 83208-02-0; **4** (Z = 4′-F), 83208-03-1; **4** (Z = 4′-H), 20615-38-7; **4** (Z = 5′-F), 83208-04-2; **4** (Z = 5′-CF$_3$), 83208-05-3; **5** (Z = 4′-CH$_3$), 83208-06-4; **5** (Z = 4′-F), 51788-85-3; **5** (Z = 5′-F), 83208-07-5; **5** (Z = 5′-CF$_3$), 83208-08-6.

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[14] For a fuller understanding of the effect of steric inhibition of resonance on the ^{13}C NMR shifts of carbocations, it may be desirable to run systems in which steric effects can be larger than in the present system, as in *o-tert*-butylcumyl cations. Very large effects of such *tert*-butyl substituents have been observed in a number of systems (see Harff, G. A.; Sinnema, A.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 71 and references cited therein, as well as Tanida, H.; Matsumura, H. *J. Am. Chem. Soc.* **1973**, *95*, 1586).

[15] Accompanying paper in this issue.

[16] We have observed similar deviations in the plot of the equilibrating 2-aryl-3-methyl-2-butyl cations. These results will be reported shortly.

[17] Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Fiske, P. R.; Rowe, J. E.; Sadek, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 753.

[18] Mawdsley, E. A.; Berlin, K. D. *Org. Prep. Proced. Int.* **1974**, *6*, 169.

[19] Ziegler, C. B., Jr.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2941.

[20] Brown, H. C.; Inukai, T. *J. Am. Chem. Soc.* **1961**, *83*, 4825.

[21] Kelly, D. P.; Brown, H. C. *Aust. J. Chem.* **1976**, *29*, 957.

Structural Effects in Solvolytic Reactions. 42. Effect of Increasing Electron Demand on the Carbon-13 Nuclear Magnetic Resonance Shifts for Substituted 9-Methyl-9-anthracenium Cations. Evidence for the Unimportance of Steric Hindrance to Coplanarity in Causing Anomalous Carbon-13 Nuclear Magnetic Resonance Shifts

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Received April 13, 1982

A series of substituted 9-methyl-9-anthracenium cations were prepared in FSO$_3$H/SO$_2$ClF at −78 °C and their ^{13}C NMR shifts were measured at −80 °C. The $\Delta\delta C^+$ shifts observed for the electron-donating substituents correlate linearly against the σ^{C^+} constants. However, the data observed for the electron-withdrawing substituents deviate upward from the straight line defined by the data of electron-donating substituents, similar to the deviation observed for the 1-aryl-1-phenyl-1-ethyl carbocations. The deviation observed in the latter case was previously attributed to steric inhibition of coplanarity. However, comparison of the behavior of this system with that of the 9-methyl-9-anthracenium system casts doubt upon this explanation.

Recently, we proposed new σ^{C^+} constants to correlate the C$^+$ shifts of benzylic carbocations.[1] The C$^+$ shifts of several simple aryldialkyl carbocations, such as 1-aryl-1-cyclopentyl cations, correlate linearly against these σ^{C^+}

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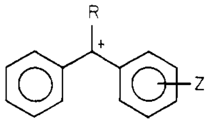
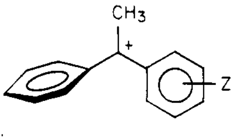
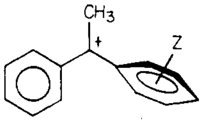
constants.[2-5] However, the C$^+$ shifts observed for the 1-aryl-1-phenylethyl cations (**1**, R = CH$_3$) and arylphenylmethyl cations (**1**, R = H) fail to correlate linearly against the σ^{C^+} constants.[6] The $\Delta\delta C^+$ values ($\Delta\delta C^+ = \delta C^+_H - \delta C^+_Z$) observed for the electron-withdrawing derivatives deviate upward from the straight line defined by the data observed for the electron-donating derivatives.



1, R = CH$_3$, H



2, Z = *p*-OCH$_3$ to Z = H



3, Z = H to Z = 3,5-(CF$_3$)$_2$

Farnum and co-workers previously observed similar deviation in the plot of the C$^+$ shifts observed for the 1-aryl-1-phenylethyl carbocations (**1**, R = CH$_3$) against the C$^+$ shifts observed for the 1-aryl-1-cyclopentyl cations.[7] They suggested that the deviation is observed in this system because of the difficulty for the aryl rings to achieve coplanarity with the cationic carbon center to attain maximum resonance interactions. It was suggested that steric hindrance to coplanarity in this system must force the less stabilizing aryl group out of coplanarity (**2** and **3**), causing less resonance interaction for the twisted ring resulting in the observed deviation. However, the excellent correlation observed in the case of *o*-methyl-*tert*-cumyl system casts doubt upon this explanation.[8]

There are other possible explanations for the observed deviations other than steric inhibition of coplanarity. In some systems there is the possibility of a rapid equilibration between tertiary and secondary carbocations that becomes important only with strongly electron-withdrawing substituents.[8] Another possibility is enhanced electron supply from certain organic moiety.[6] A fourth is inductive π polarization, as recently proposed by Brownlee and co-workers.[9]

For example, we recently pointed out that the upfield shifts and deviations in the σ^{C^+}–$\Delta\delta C^+$ plots observed for the electron-withdrawing derivatives in some aryl carbocations are similar to the upfield shifts observed for the substituted benzene derivatives with conjugating side chain.[6] For example, in meta- and para-substituted acetophenones, the carbonyl carbon undergoes upfield shift when the benzene ring is substituted with electron-withdrawing groups.[9] Brownlee and co-workers suggested that such upfield shifts are due to the inductive π polarization of the conjugating side chain by the electron-withdrawing aryl groups.[9] It follows that the upfield shifts and deviations in the σ^{C^+}–$\Delta\delta C^+$ plots observed for the electron-withdrawing derivatives of some aryl carbocations may be also due to such inductive π polarization of the stabilizing groups in these cations.

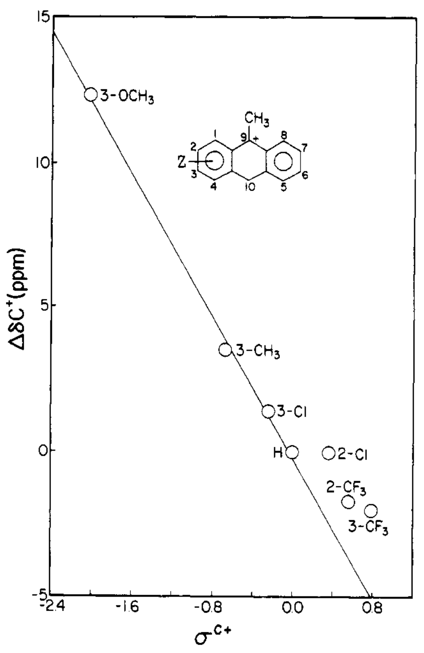
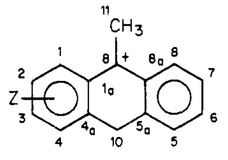


Figure 1. A plot of σ^{C^+} against $\Delta\delta C^+$ values for the 2- or 3-substituted 9-methyl-9-anthracenium cations **4**: slope (ρ^{C^+}) = −6.1 and correlation coefficient (r) = 0.999 (for electron-donating substituents only).

Accordingly, it appeared desirable to examine the importance of steric inhibition of coplanarity.

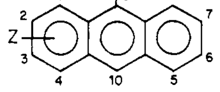
A suitable system for such an examination appeared to be the 2- or 3-substituted 9-methylanthracenium (**4**) system where geometry change with different substituents should not be significant because of the rigidity of the ring system.



4

Results and Discussion

The unsubstituted 9-methyl-9-anthracenium ion (**4**, Z = H) was previously prepared and examined by Olah and co-workers.[10] The authors prepared this ion by protonation of 9-methylanthracene (**5**, Z = H) in FSO$_3$H/SO$_2$ClF medium. We prepared the 2- or 3-substituted 9-methylanthracene derivatives (**5**) from the corresponding 3- or 4-substituted benzoyl-2′-benzoic acid (**6**) in five steps following a general method reported for the synthesis of the 9-methylanthracene derivatives.[11] The corresponding



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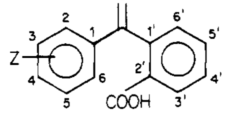

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Z = 3-OCH$_3$, 3-CH$_3$, 3-Cl, 3-H, 2-Cl, 2-CF$_3$, 3-CF$_3$

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[1] Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956.

[2] Brown, H. C.; Periasamy, M.; Liu, K.-T. *J. Org. Chem.* **1981**, *46*, 1646.

[3] Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3161.

[4] Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3166.

[5] Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1982**, *47*, 5.

[6] Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089.

[7] Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847.

[8] Preceding paper in this issue.

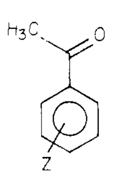
[9] Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Fiske, P. R.; Rowe, J. E.; Sadek, M. *J. Chem. Soc. Perkin Trans. 2* **1981**, 753.

[10] Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299.

carbocations 4 were prepared in FSO_3H/SO_2ClF at −78 °C and the ^{13}C NMR shifts were measured at −80 °C. The data are summarized in Table I.

The $\Delta\delta C^+$ shifts observed for the electron-donating derivatives correlate nicely against the σ^{C^+} values (Figure 1). However, the data observed for the electron-withdrawing derivatives exhibit an upward deviation similar to the deviation observed for the 1-aryl-1-phenylethyl (1, R = CH_3) carbocations.[6,7] The deviation observed for the 1-aryl-1-phenylethyl cations (1, R = CH_3) has been attributed to the progressive change in the geometry (2 to 3) with increasing electron demand because of steric hindrance to coplanarity.[7] In system 4, the aryl rings are locked in a ring skeleton. Consequently, change in the geometry cannot have a significant role in the variation of ^{13}C NMR shifts for system 4. Yet the same kind of deviations are observed for both 1 and 4. Accordingly, one has to look for some other explanation to account for the deviation in the σ^{C^+}–$\Delta\delta C^+$ plots observed for these systems.

In this regard, it may be of interest to consider the ^{13}C NMR behavior of some neutral, side-chain conjugated benzene derivatives. Brownlee and co-workers observed that the chemical shift of the carbonyl carbon atom in substituted acetophenones 7 undergoes upfield shift in electron-withdrawing derivatives.[9]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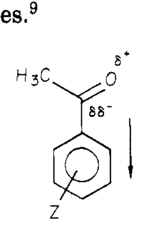
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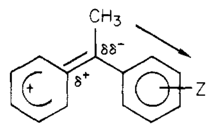
For example, the carbonyl carbon atom shift undergoes a downfield shift by 1.2 ppm from Z = p-OCH_3 to Z = H and an upfield shift by 1.2 ppm from Z = H to Z = p-CF_3. Brownlee and co-workers attributed such upfield shifts observed for the electron-withdrawing derivatives to the inductive π polarization shown in 8.[9]

Such an inductive π polarization is also possible for the aryl cations under consideration (9 and 10). Such π polarization would cause more shielding (upfield shift) for the C^+ carbon atoms. This could lead to the upward deviations in the σ^{C^+}–$\Delta\delta C^+$ plot.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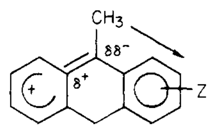
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Comparison of the data observed for the substituted acetophenones (7), 1-aryl-1-phenyl-1-ethyl cations (1), and substituted 9-methyl-9-anthracenium cations (4) indicates that the π polarization that causes the upward deviations in the σ^{C^+}–$\Delta\delta C^+$ plots arises because of the double bond *character between the C^+ carbon atom and the conjugating* atom (8, 9, and 10). Conversely, the upward deviations in the σ^{C^+}–$\Delta\delta C^+$ plot should occur for electron-withdrawing derivatives when there is significant double bond character between the C^+ carbon atom and the conjugating or hyperconjugating carbon atom. Accordingly, it is not surprising to observe[6] such deviations in the σ^{C^+}–$\Delta\delta C^+$ plot for the systems 11 and 12 because in these cases cyclo-

Table I. ^{13}C NMR Shifts[a] of Substituted 9-Methyl-9-anthracenium Cations 4 in FSO_3H/SO_2ClF at −80 °C

substituent (Z)	chemical shift															
	C_9^+	C_{CH_3}	$C_{10}(CH_2)$	C_Z	C_1	C_{1a}	C_2	C_3	C_4	C_{4a}	C_{5a}	C_5	C_6	C_7	C_8	C_{8a}
3-OCH_3	188.8	19.8	38.0	58.4	140.1	129.0	121.5	174.9	114.5	158.9	147.2	130.9	139.7	130.1	133.4	132.7
3-CH_3	197.6	20.8	38.5	25.5	136.1	132.3	132.7	161.1	131.6	154.1	151.3	130.6	143.2	130.8	135.0	133.5
3-Cl	199.7	21.5	38.6		137.1	132.6	131.8	153.2	131.1	154.0	152.8	131.1	145.1	131.1	136.0	133.9
H	201.1	21.5	39.2		135.9	134.0	131.1	144.8	131.1	153.5	153.5	131.1	144.8	131.1	135.9	134.0
2-Cl	201.1	21.8	39.0		133.7	134.8	136.9	143.4	132.3	151.4	154.8	131.4	146.1	131.4	136.5	134.2
2-CF_3	202.8	22.1	39.5	123.5 (273)	132.1	134.4	b	138.6	132.1	155.2	155.2	131.7	147.2	131.5	137.0	133.5
3-CF_3	203.1	22.4	39.6	123.5 (273)	134.8	135.6	127.6 (4)	141.7 (34)	126.8 (3)	152.3	156.2	131.6	147.6	131.8	137.3	136.1

[a] In parts per million downfield from Me_4Si (capillary). The signals are assigned by comparison with the previously reported values for the unsubstituted 9-methyl-9-anthracenium cation[10] and by off-resonance experiments. ^{13}C–F coupling constants (in hertz) are in parentheses. [b] Signal too weak to measure.

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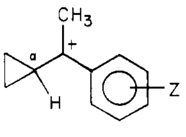
(11) Shemyahin, M. M.; Kolosov, M. N.; Hsieh, Y.-Y.; Karapetyan, M. G.; Shen, H.-Y.; Gurevich, A. I. *Izv. Akad. Nauk SSSR Ser. Khim.* **1964**, 1013–1024; *Chem. Abstr.* **1964**, *61*, 9446a.

propyl conjugation should give double bond character for the bond between C^+ and C_α carbon atoms. The 2-aryl-2-norbornyl cations (**13**) have revealed a deviation in the σ^{C^+}–$\Delta\delta C^+$ plot similar to the deviations observed for systems **1**, **4**, **11**, and **12**. The former deviation has been attributed to the "onset of σ-bridging" in the norbornyl system accompanying the introduction of electron-withdrawing substituents.[7,12] However, this explanation will not serve for **1**, **4**, **11**, and **12**. Moreover, the behavior of the C_1 and C_6 carbon atoms in 2-aryl-2-norbornyl is not consistent with the σ-bridging proposal.[6] In a σ-bridged ion, the C_6 carbon atom would be pentacoordinated and should exhibit unusual ^{13}C NMR behavior.[6] Instead, the C_6 carbon chemical shifts correlate linearly against the corresponding chemical shifts of the C_β carbon atom in the 1-aryl-1-cyclohexyl cations. Consequently, we must seek some other explanation for the observed deviation in the σ^{C^+}–$\Delta\delta C^+$ plot.



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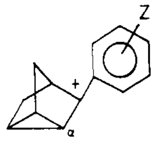

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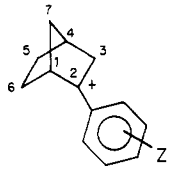
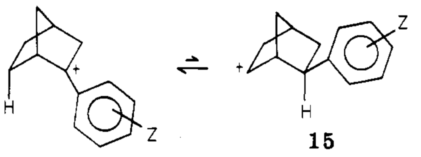
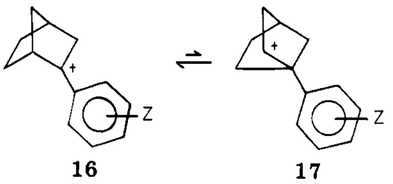


13

One possibility is the existence of a rapid equilibrium between tertiary and secondary carbocations in the 2-aryl-2-norbornyl system (**14** and **15**). An alternative equilibration could involve a Wagner–Meerwein shift (**16** and **17**). We are subjecting this possible explanation to careful scrutiny.



14 **15**



16 **17**

However, it should be pointed out that this explanation would not account for systems **1**, **4**, **11**, and **12**. Here we are apparently forced to consider either enhanced electron supply from certain organic moieties or inductive π polarization.

Experimental Section

Precursors. The 2- or 3-substituted 9-methylanthracenes **5** were synthesized in five steps from 3- or 4-substituted benzoyl-2′-benzoic acid **6** following a general method reported for the synthesis of 9-methylanthracene derivatives.[11] All of these compounds, except the derivatives Z = 3-OCH_3 and Z = 3-CF_3, are reported in the literature. The previously unknown derivatives, Z = 3-OCH_3 (mp 108–109 °C) and Z = 3-CF_3 (mp 65–66 °C), were also synthesized in the same fashion. Satisfactory analytical data (C, ±0.2; H, ±0.2; F, ±0.1) were obtained for these derivatives. All of these compounds gave ^{13}C NMR data in accordance with their structures.

Carbocations. The substituted 9-methyl-9-anthracenium cations **4** were prepared by slow addition of powdered 9-methylanthracene derivative to a solution of FSO_3H/SO_2ClF cooled to −78 °C with rapid vortex mixing. The acid concentration in the solution was 3 M. The concentration of the ion based on the precursor added was ~0.5 M. Transfer of the solution under nitrogen to an 8-mm NMR tube was achieved via a cooled double-ended syringe, as described previously.[13]

NMR Spectra. ^{13}C NMR spectra were recorded at −80 °C on a Varian CFT-20 spectrometer with 8-mm tubes containing a concentric 3-mm (o.d.) capillary tube of acetone-d_6 and Me_4Si, 8192 data points, a spectral width of 6000 Hz, and a pulse angle of 45°. Chemical shifts are in parts per million downfield from external Me_4Si.

Registry No. **4** (Z = 3-OCH_3), 83220-01-3; **4** (Z = 3-CH_3), 83220-02-4; **4** (Z = 3-Cl), 83220-03-5; **4** (Z = H), 83220-04-6; **4** (Z = 2-Cl), 83220-05-7; **4** (Z = 2-CF_3), 83220-06-8; **4** (Z = 3-CF_3), 83220-07-9; **5** (Z = 3-OCH_3), 83220-08-0; **5** (Z = 3-CF_3), 83231-99-6.

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(12) Olah, G. A.; Berrier, A. L.; Prakash, G. K. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1998.

(13) Kelly, D. P.; Brown, H. C. *Aust. J. Chem.* **1976**, *29*, 957.

Synthesis of Vincamine

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Received May 17, 1982

A five-step procedure for the conversion of a well-known indoloquinolizidine into the alkaloid (+)-vincamine is described. The vital step of the synthesis involves the introduction of a side chain, subsequently becoming the functionalized part of the fifth ring of the base, by way of the alkylation of an enamine with methyl bromopyruvate 2,4-dinitrophenylhydrazone.

Vincamine (**1a**), a major alkaloid of the common plant *Vinca minor* L., has gained importance in recent years as a drug in the treatment of cerebral, vascular, and metabolic diseases.[1] Its isolation in crystalline form in 1953[2] led to

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