Lewis- or Brønsted-acid assisted formation of open-chain vinamidinium salts from *N,N′*-diarylformamidines and acetone

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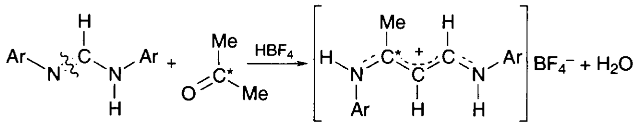
An unorthodox reaction of ArNC(H)N(H)Ar (Ar = phenyl, tolyl) with acetone in the presence of a Lewis or Brønsted acid entails the cleavage of a C–N bond of the formamidine; subsequent incorporation of two carbon atoms of the acetone molecule yields the vinamidinium species *N*-[3-(phenylamino)-2-propenylidene]benzenaminium tetrafluoroborate 1, or the corresponding *p*-tolyl analogue 2.

Amidines and their corresponding anions, [RNC(R)NR]$^-$, are known to coordinate to transition metal atoms in a variety of modes.[1] A few examples are known where, instead of simply functioning as a ligand, an amidine reacted in the presence of a metal atom to be transformed, either by combining with another molecule or by fragmentation, to give a different ligand.[2] We report here a new type of reaction that has led to the the synthesis of two vinamidinium salts,† in which Ar is phenyl (**1**) or *p*-tolyl (**2**). From the reaction of ArNC(H)N(H)Ar (Ar = phenyl, *p*-tolyl) and acetone in the presence of a Lewis acid such as Mn^{2+}, Zn^{2+} or H^+ and an anion such as BF_4^- the reaction proceeds as shown in Scheme 1. This reaction is significant because: (*i*) it is an example of an uncommon reaction in which an amidine or amidinium species undergoes cleavage of a C–N bond in the presence of a Lewis acid; (*ii*) subsequent incorporation of two carbon atoms of an acetone molecule produces the vinamidinium species in a one-pot synthesis, contrary to previous preparations of related compounds[3] which typically required several steps and (*iii*) the reaction appears to be general with respect to both the formamidine and the ketone. Scheme 1 shows the overall reaction as promoted by HBF_4.



Scheme 1

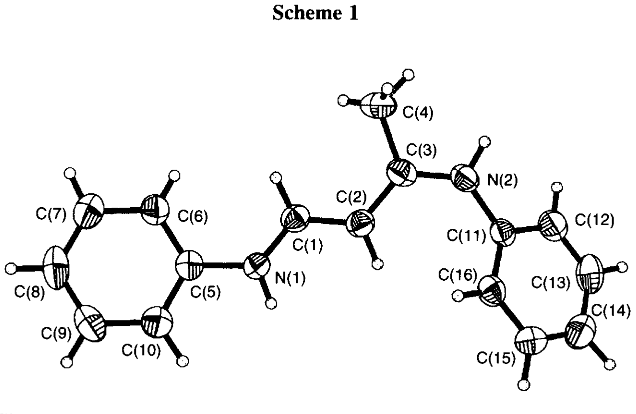


Fig. 1 A drawing of the cation of **1** showing the atom labelling scheme. Selected bond lengths (Å) and angles (°) for **1** and **2** (square brackets) N(1)–C(5) 1.414(5) [1.421(7)], N(1)–C(1) 1.310(5) [1.337(7)], C(1)–C(2) 1.372(5) [1.368(8)], C(2)–C(3) 1.392(5) [1.399(7)], C(3)–N(2) 1.336(5) [1.319(6)], N(2)–C(11) 1.419(5) [1.411(6)], N(1)–C(1)–C(2) 124.3(4) [124.1(6)], C(1)–C(2)–C(3) 123.5(4) [121.8(6)], C(2)–C(3)–N(2) 123.4(4) [123.8(5)].

^{1}H NMR data for **1** and **2** are consistent with their formulation as open-chain vinamidinium[4] cations; and this was confirmed for both by X-ray crystallographic results.‡ Fig. 1 shows a drawing of the cation in **1**. The cation of **2** is very similar to that of **1** and those of the few other open-chain vinamidinium cations which have been crystallographically characterized.[5] Cyclic vinamidinium structures such as derivatives of diazepinium[6] and other more complex species[7] are also known.

In both **1** and **2** the positive charge is delocalized along the NCCCN chain as indicated by the short C–C and C–N distances. The conformation of such chains can be described as all-*trans* ('W'), as opposed to the all-*cis* ('U') conformation found in the diazepinium cations mentioned earlier.

A labelling experiment carried out using $Me_2{}^{13}CO$ clearly demonstrated that the ^{13}C label is incorporated as shown in Scheme 1. The ^{1}H NMR of this sample is identical to that of the unlabelled compound except that a weak signal at δ 172.3 was greatly enhanced in the ^{13}C NMR spectrum of the labelled product. This signal is in the range expected for a carbon atom of an open-chain vinamidinium ion.[5f]

We are currently working to optimize the yields of this type of reaction and are carrying out experiments designed to provide insight into the mechanism of formation of vinamidinium salts *via* the reactions of formamidines with ketones. Very probably, enolization of the ketone is an early step, but subsequent steps remain to be elucidated.

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Footnotes

† *Preparations*: **2**. To a mixture of Zn powder (200 mesh) (0.05 g, 0.76 mmol) and 2 equiv of $NOBF_4$ (0.179 g, 1.53 mmol) cooled in a liquid–N_2 bath was added 5 ml of acetone. The reaction mixture was slowly allowed to warm to room temperature. Upon warming, rapid evolution of NO(g) was observed and the reaction solution first became yellow–green and finally yellow. After 2 h, *N,N′-p*-tolylformamidine (0.340 g, 1.82 mmol) was added to the solution. Gradually the solution turned orange–red. After 24 h, the reaction mixture was filtered in air to remove the unreacted Zn powder. The red solution was concentrated to approx. 3 ml and diethyl ether was added slowly to the solution. The resulting yellow precipitate was filtered and washed several times with benzene and diethyl ether. The product was recrystallized by slow diffusion of diethyl ether into an acetone solution of the product. The reactions were also done using Mn powder or $HBF_4{\cdot}Et_2O$. Isolated yields varied from 20 to 30%. Anal. Calc. for $C_{18}H_{21}BF_4N_2$: C, 61.39; H, 6.01; N, 7.95. Found: C, 61.40; H, 5.83; N, 7.73%. IR (Nujol)/cm^{-1}: 3303s, 1640s, 1615t, 1589s, 1562s, 1509s, 1348s, 1336s, 1321s, 1291s, 1271s, 1253s, 1215m, 1188w, 1128m, 1043s (br), 991s, 861m, 832m, 823m, 811s, 766m, 730m, 640w, 560m, 508s. ^{1}H NMR (CD_3CN): δ 2.31 (s, 3H), 2.39 (s, 3H), 2.51 (br s, 3H), 5.85 (d, *J* 12.2 Hz, lH), 7.14–7.36 (m, 8H), 8.33 (d, *J* 12.2 Hz, lH), 9.38 (br, 2H). ^{13}C NMR (CD_3CN): δ 20.9, 21.2, 126.1, 131.3, 134.5, 137.0, 137.2, 139.8. Electronic absorption spectrum (acetone): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 368 (34 000), 300 (4130), 290 (3520), 240 (10 040). Mass spectrum (FAB$^+$, thioglycerol–acetonitrile): *m*/*z* 265 ([M − BF_4], 100%), 158 (24%), 132 (17%).

1. Compound **1** was prepared using analogous preparative procedures as for **2**. Anal. Calc. for $C_{16}H_{17}BF_4N_2$: C, 59.29; H, 5.29; N, 8.64. Found: C, 58.99; H, 5.28; N, 8.64%. IR (Nujol)/cm^{-1}: 1640s, 1615w, 1591s, 1562s, 1510s, 1353m, 1326m, 1305m, 1205m, 1159w, 1055s (br), 852m, 754s, 722m, 689m, 657w, 608, 521w, 508m.

‡ X-Ray data for both **1** and **2** were obtained on an Enraf-Nonius FAST area detector diffractometer at −60 °C. Both structures were solved *via* direct methods and were refined on $F_o{}^2$ using all data. In each case the refinement included anisotropic displacement parameters for the non-hydrogen atoms, and the positional and isotropic displacement parameters for the hydrogen atoms.

Crystal data: **1**, dimensions 0.4 × 0.3 × 0.2 mm, $C_{16}H_{17}BF_4N_2$, M = 324.13, monoclinic, space group $C2/c$, a = 14.811(2), b = 11.887(1), c = 19.020(1) Å, β = 109.37(1)°, Z = 8, D_c = 1.363 g cm^{-3}, μ(Mo-Kα) = 0.113 mm^{-1}. 1421 Unique data were used to refine the model, giving final residuals based on $F_o{}^2$ of 0.142 (all data) and 0.118 [for $I > 2\sigma(I)$], and based on F_o of 0.077 (all data) and 0.049 [for $I > 2\sigma(I)$].

2, Dimensions 0.5 × 0.3 × 0.3 mm, $C_{18}H_{21}BF_4N_2$, M = 352.18, triclinic, space group $P\bar{1}$, a = 9.143(2), b = 12.396(4), c = 9.055(2) Å, α = 94.92(2), β = 117.46(2), γ = 74.02(2)°, Z = 2, D_c = 1.338 g cm^{-3}, μ(Mo-Kα) = 0.108 mm^{-1}. 1525 Unique reflections were used in the refinement, resulting in final residuals based on $F_o{}^2$ of 0.203 (all data) and 0.176 [for $I > 2\sigma(I)$], and based on F_o of 0.084 (all data) and 0.067 [for $I > 2\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/258.

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