Letters to the Editor

Values of pK_{R^+} for coordinated propargyl cations $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC\equiv CCR^1R^2)]^+$

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Presently, two series of metal-stabilized carbocations, which contain only H atoms or alkyl groups bonded to the center of the carbocation (to the C atom that bears a positive charge; hereinafter, C_α) and for which the values of pK_{R^+} were measured, are known. In the first series, which is a series of ferrocenylmethyl cations, pK_{R^+} increases from −1.28 for $FcCH_2^+$ to −0.01 for $FcCMe_2^+$, which is indicative of an increase in the stability in this order.[1] In the second series, $[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^3\text{-}(HC\equiv CCR^1R^2)]^+$, pK_{R^+} remains virtually unchanged (it changes from −6.8±0.02 for $R^1 = R^2 = H$ to −7.2±0.02 for $R^1 = R^2 = Me$).[2] More recent studies cast doubt on this statement.[3] Unfortunately, the structural data for the above-mentioned series of carbocations are unavailable. Therefore, the dependence of the values of pK_{R^+} on the structural parameters of the cations, in particular, on the metal—C_α distance, cannot be studied.

The series of coordinated propargyl cations were the first metal-stabilized carbocations studied by X-ray diffraction analysis: $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}(HC\equiv CCR^1R^2)]^+BF_4^-$ (**1**) ($R^1 = R^2 = H$ (**1a**); $R^1 = H$, $R^2 = Me$ (**1b**); $R^1 = R^2 = Me$ (**1c**)).[4,5] An increase in the Mo—C_α (*R*) distance from 0.2439 nm in **1a** to 0.274 nm in **1c** is indicative of a decrease in the Mo—C_α interaction in this series. We measured the values of pK_{R^+} potentiometrically (a 50% aqueous MeCN solution, 20 °C). They are 4.82±0.06, 3.81±0.04, and 3.12±0.06 for cations **1a—c**, respectively. These data suggest that cations **1** are substantially more stable than ferrocenylmethyl cations and are only slightly less stable than cyclopropenyl cations.[6] Therefore, in the case of cations **1**, it was found for the first time that the replacement of the H atom at the C_α atom by the methyl group led to a *decrease* rather than to an increase in the stability (as was observed previously in the case of all metal-stabilized carbocations). The values of pK_{R^+} linearly depend on *R*. This dependence can be described by the following equation: $pK_{R^+} = 18.61 - 56.6R$. In conclusion, it should be mentioned that the stability of noncoordinated propargyl cations changes in the usual order, namely, $[HC\equiv C=CH_2]^+ < [HC\equiv C=CHMe]^+ < [HC\equiv C=CMe_2]^+$, as follows from the results of measurements of the energy of heterolytic cleavage of the bond in the gaseous phase.[7]

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Reaction of *N*-cyanoamines with polyfluorocarbonyl compounds

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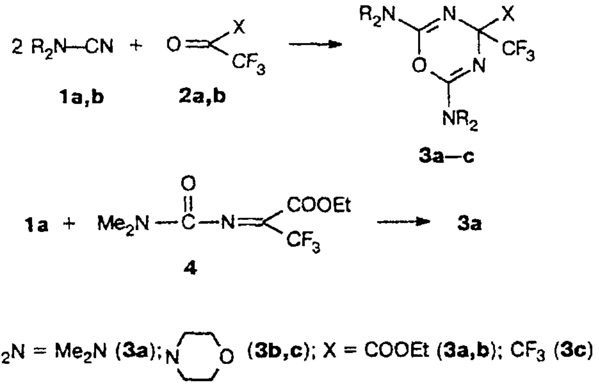
In a study of reactions of *N*-cyanodimethylamine (**1a**) and *N*-cyanomorpholine (**1b**) with ethyl 3,3,3-trifluoropyruvate (**2a**) and hexafluoroacetone (**2b**), we discovered a new type of transformation of cyanoamines, which give 1,3,5-oxadiazines (**3a—c**) with polyfluorocarbonyl compounds.



The structures of the compounds obtained were proved by ^1H and ^{19}F NMR spectroscopy and by data of elemental analysis; the structure of **3a** was confirmed by its alternative synthesis from **1a** and ethyl 2-*N*-(*N*,*N*-dimethylcarbamoyl)imino-3,3,3-trifluoropropionate (**4**) using the previously described procedure.[1]

Ethyl 2,6-bis(dimethylamino)-4-trifluoromethyl-1,3,5-oxadiazine-4-carboxylate (3a). *A.* A mixture of cyanide **1a** (0.01 mol) and ketone **2a** (0.05 mol) in 50 mL of anhydrous ether was kept for 24 h at ~20 °C. The ether was evaporated, and the residue was recrystallized from a hexane—benzene mixture (10 : 1) to give oxadiazine **3a**, yield 89%, m.p. 90—92 °C. Found (%): C, 42.69; H, 5.28; N, 17.83. $C_{11}H_{17}F_3N_4O_3$. Calculated (%): C, 42.60; H, 5.53; N, 18.07. ^1H NMR ($CDCl_3$), δ: 1.28 (t, 3 H, $\underline{Me}CH_2$); 2.95 (s, 12 H, MeN); 4.22 (q, 2 H, CH_2O). ^{19}F NMR ($CDCl_3$), δ: −3.11.

B. A mixture of compound **1a** (0.01 mol) and acylimine **4** (0.01 mol) in 50 mL of anhydrous ether was kept for 24 h at ~20 °C. The ether was evaporated, and the residue was recrystallized from a hexane—benzene mixture (10 : 1) to give oxadiazine **3a**, yield 92%, m.p. 90—92 °C. The NMR characteristics of the product were identical with those of the sample of **3a** prepared by procedure *A*.

Ethyl 2,6-bis(morpholino)-4-trifluoromethyl-1,3,5-oxadiazine-4-carboxylate (3b) was prepared similarly to compound **3a** (procedure *A*). Yield 87%, m.p. 91—92 °C. Found (%): C, 45.90; H, 5.38; N, 14.63. $C_{15}H_{21}F_3N_4O_5$. Calculated (%): C, 45.71; H, 5.37; N, 14.21. ^1H NMR ($CDCl_3$), δ: 1.30 (t, 3 H, $\underline{Me}CH_2$); 3.44 (m, 4 H, CH_2N); 3.70 (m, 4 H, CH_2O); 4.24 (q, 2 H, CH_2O). ^{19}F NMR ($CDCl_3$), δ: −2.95.

2,6-Bis(morpholino)-4,4-bis(trifluoromethyl)-1,3,5-oxadiazine (3c). A mixture of cyanide **1b** (0.01 mol) and ketone **2b** (0.05 mol) in 50 mL of anhydrous ether was kept in a closed vessel for 24 h at ~20 °C. The ether was evaporated, and

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