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Reaction of Some Strong N-Bases with Chloropentafluorobenzene in the Presence of Water Molecules

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Products of reactions between chloropentafluorobenzene and strong N-bases (DBN, DBU, TBD, and MTBD) in polar aprotic solvents and in the presence of water were isolated and identified by analytical and spectroscopic methods. The products of these dehydrohalogenation reactions are apropriate lactams, and if the TBD N-base is used, a condensation occurs with formation of benzimidazole derivative. All the products are not formed directly in the nucleophilic substitution by N-bases but after the hydrolyses of the N-bases with formation of amines known as hard nucleophiles.

Introduction

The amidines 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)[1] and guanidines 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)[2] and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD)[3] belong to very strong N-bases with low nucleophilicity.[4−7] TBD and MTBD molecules in acetonitrile are very strong N-bases, and their pK_a values are 24.97 and 24.70, respectively.[6] The pK_a values of the amidines DBU and DBN are 24.33 and 23.79, respectively.[6]

Amidines and guanidines are very important agents in the deprotonation reactions of weak O−H,[8−12] N−H,[13−15] and C−H[16−18] acids, whereas after protonation all of them, except for MTBD, can form homoconjugated complexes.[19] Furthermore, in our previous papers we have demonstrated that MTBD can form hydrogen-bonded chains with phenols,[8−12,20,21] biphenols, and NH acids in nonpolar aprotic solvents as well as in the solid state. The same is true in the case of TBD but the respective complexes have much more complicated structures, both in solution and in the solid state.[22−24]

Recently, we have also demonstrated that the reaction between the MTBD and fluorinated benzoic acid yielded fluorinated benzene.[25]

In this paper, we show that the strong N-bases studied can also react with chloropentafluorobenzene to yield various products, identified by spectroscopic methods. Detailed recognition of the reactions observed is very important in all studies in which the strong N-bases are used in the presence of water.

Experimental Section

Chloropentafluorobenzene and the N-bases DBU, DBN, TBD, and MTBD were commercial products and were used without any purification.

Synthesis. Chloropentafluorobenzene (0.01 mol) was dissolved in acetonitrile (25 mL), and then stoichiometric amounts of the N-base and water (0.01 mol) were added. The solution was heated under reflux for 0.5 h. The solvent was evaporated in a vacuum, and the oily residue was extracted with diethyl ether (20 mL). The organic layer was dried with anhydrous

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TABLE 1. Elementary Analysis, Melting Points, and High-Resolution MS Data of Compounds 1−5

		elemental analysis		MS		
compd	yield (%)	calcd	found	calcd	found	mp (°C)
1	46	C, 47.54 H, 4.56 N, 11.88	C, 47.52 H, 4.64 N, 11.91	353.09180 $C_{14}H_{16}ON_3F_4{}^{35}Cl$	353.08951	96.0−96.5 white crystals
2	46	C, 47.54 H, 4.56 N, 11.88	C, 47.32 H, 4.48 N, 11.53	353. 09180 $C_{14}H_{16}ON_3F_4{}^{35}Cl$	353.09261	88.0−89.5 white crystals
3	94	C, 48.84 H, 4.10 N, 13.14	C, 48.81 H, 4.10 N, 13.17	319.06992 $C_{13}H_{13}ON_3F_3{}^{35}Cl$	319.06867	189.2−189.4 white crystals
4	91	C, 51.07 H, 4.86 N, 7.94	C, 51.07 H, 5.02 N, 7.99	352.09656 $C_{15}H_{17}ON_2F_4{}^{35}Cl$	352.09537	76.5−77.0 white crystals
5	95	C, 48.09 H, 4.04 N, 8.63	C, 48.09 H, 4.27 N, 8.69	324.06525 $C_{13}H_{13}ON_2F_4{}^{35}Cl$	324.06418	72.0−73.0 white crystals

TABLE 2. UV−vis and FT-IR Data of Compounds 1−5

	UV−vis data		FT-IR data	
compd	λ_{max} (nm)	ϵ	ν(N−H)[a] (cm^{-1})	ν(C=O))cm^{-1})
1	269.0	9458	3293b, 3218b, 3063b	1659
2	247.0	27272	3310b	1629
3	230.0 354.0	12238 2727	3340sh	1721
4	247.0	22058	3294b	1630
5	247.0	21327	3311b	1675

[a] b, broadened; sh, sharp.

sodium sulfate and filtered, and then diethyl ether was evaporated. The crude product was purified by column chromatography on silica gel, using ether−hexane or ether−acetone mixture as an eluent. The purity of the fraction was checked by TLC under similar conditions.

General Methods. Elemental analysis and melting point determination were performed using standard methods (Table 1).

UV−vis Spectra. The UV−vis spectra were recorded in CH_3CN using a 1 cm cell thick and the samples of the concentration 5×10^{-4} mol dm^{-3}. The data of these spectra are collected in Table 2.

NMR Measurements. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a spectrometer at 300.075, 75.461, and 282.352 MHz, respectively, in 0.1 M $CDCl_3$ solutions, in 5 mm tubes. The chemical shifts were measured with respect to an internal standard (TMS for ^1H and ^{13}C NMR spectra; $CFCl_3$ for ^{19}F NMR spectra δ 0.00 ppm).

Mass Spectrometry. High-resolution MS spectra were obtained on two sector mass spectrometer of the B/E geometry using a peak matching technique. Elemental compositions of the ions discussed were determined with an error of less than 10 ppm in relation to perfluorokerosene at a resolving power of 10000.

FT-IR Measurements. The FT-IR spectra of compounds **1**−**5** were recorded in KBr pellets (1.5/200 mg) at 300 K on a spectrometer equipped with DTGS detector (resolution of 2 cm^{-1}).

PM5 Calculations. PM5 semiempirical calculations were performed using the Win Mopac 2002 program.[26] The full geometry optimization was carried out without any symmetry constraints.[27]

Results and Discussion

The substrates of the studied reactions are shown in Chart 1.

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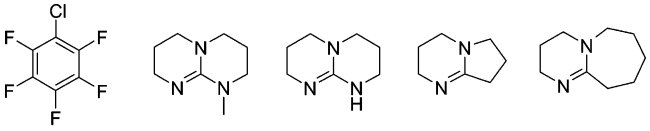
CHART 1. Structures of Studied Compounds



Synthesis. The reaction between chloropentafluorobenzene with MTBD, DBU, and DBN in the presence of water yielded para-substituted chloro-2,3,5,6-terafluorobenzenes (**1**, **2**, **4**, and **5**). In the reaction of chloropentafluorobenzene with TBD, two fluorine atoms are substituted giving a novel compound **3**. Furthermore, only in the reaction with MTBD two isomeric products were isolated and identified (**1** and **2**). In all cases, the bicyclic structure of the N-base was cleaved as shown in Scheme 1. The same scheme gives also the numbering of the atoms.

The structures of compounds **1**−**5** were determined by ^1H, ^{13}C, and ^{17}F NMR methods, the elemental analysis, UV−vis and FT-IR spectroscopies, and determination of molecular ions with the use of high-resolution MS method (Tables 1 and 2).

NMR Measurements. The chemical shifts and coupling constants observed in the ^1H, ^{13}C and ^{17}F NMR spectra of compounds **1**−**5** are collected in Tables 3−6, respectively.

In the ^1H NMR spectra of compounds **1**, **2**, **4**, and **5**, the signals of typical $A_2M_2X_2$ spin systems are observed. The most shifted signals of this system are CH_2 protons from the groups bonded with the N atoms involved in the aliphatic chain. The scalar coupling of the CH_2 proton signals (triplet, quintet, triplet) shows that they are not involved in the cyclic ring but in the linear chain. In contrast, the CH_2 proton signals from the cyclic part of these molecules show more complicated spin−spin couplings due to the presence of protons at axial and equatorial positions. Furthermore, the coupling of the C^7 carbon atom and C^7H_2 protons with fluorine atom in the respective spectra is found, indicating the binding of this methylene group to the nitrogen atom bonded to the aromatic ring. In the case of compound **1**, the location of the methyl group on this N atom is the reason for the coupling of the carbon atom and the protons with the fluorine atoms at positions 3 and 5. Because of this

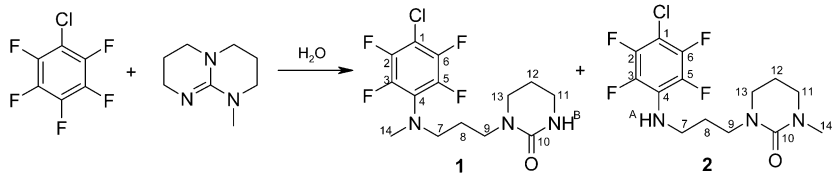
TABLE 3. ^{1}H NMR Chemical Shift (ppm) and Coupling Constants (Hz) for Compounds 1−5

	^{1}H NMR data[a]									
compd	H^7	H^8	H^9	H^{11}	H^{12}	H^{13}	H^{14}	H^{15}	NH^A	NH^B
1	3.17 t $^3J_{HH} = 7.4$	1.80 qu $^3J_{HH} = 7.4$	3.35 t $^3J_{HH} = 7.4$	3.29 dt $^3J_{HH} = 5.9$ $^3J_{HH} = 2.8$	1.98 qu $^3J_{HH} = 5.9$	3.25 t $^3J_{HH} = 5.9$	2.93 t $^5J_{HF} = 1.2$			5.34 bt $^3J_{HH} = 2.8$
2	3.38 q $^3J_{HH} = 6.3$	1.71 qu $^3J_{HH} = 6.3$	3.44 t $^3J_{HH} = 6.3$	3.26 t $^3J_{HH} = 5.8$	1.98 qu $^3J_{HH} = 5.8$	3.29 t $^3J_{HH} = 5.8$	2.96 s		5.31 bt	
3	4.4 and 3.9 m	1.5 m	2.9 and 2.5 m	4.4 and 3.9 m	1.5 m	2.9 and 2.5 m				−0.17 tt $^3J_{HH} = 12.1$ $^3J_{HH} = 4.2$
4	3.5 m	1.7 m	3.3 m	2.62 t $^3J_{HH} = 6.1$	1.7 m	1.7 m	1.7 m	3.3 m	5.25 bt	
5	3.7 m	1.74 qu $^3J_{HH} = 6.3$	3.7 m	2.44 t $^3J_{HH} = 7.9$	2.07 qu $^3J_{HH} = 7.9$	3.7 m			4.95 bt	

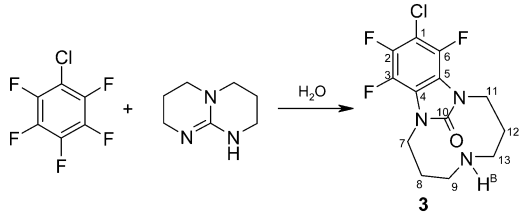
[a] s, singlet; t, triplet; qu, quintet; m, multiplet; b, broad.

SCHEME 1. Reactions of Chloropentafluorobenzene with Guanidine and Amidine Base

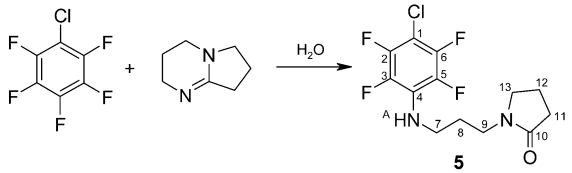
Reaction with MTBD



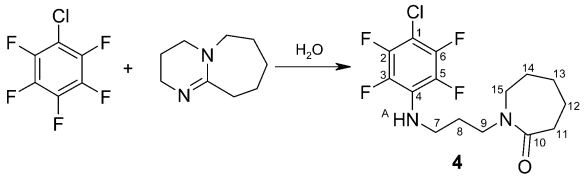
Reaction with TBD



Reaction with DBN



Reaction with DBU



coupling, triplets are observed in the respective ^{1}H and ^{13}C NMR spectra.

The NH protons signals in the ^{1}H NMR spectra of compounds **2**, **4**, and **5** shown a strongly broadened triplet structure because of their scalar coupling with ^{19}F atoms at the 3 and 5 positions. This coupling disappears after fluorine frequency decoupling. For compound **1**, such a coupling is not observed because there are no NH group at the aromatic ring.

In the ^{13}C NMR spectra of all compounds, most characteristic are the signals assigned to the carbonyl carbon atoms. In the spectra of compounds **1**−**3**, the corresponding chemical shifts of the carbonyl carbon atom signals reaches about 155 ppm suggesting a urea group in their structures. In contrast to the above spectra, in the spectra of compounds **4** and **5** the signals of the carbonyl groups are observed at about 176 ppm suggesting an amide group in the molecular structure. This interpretation is further confirmed by the carbonyl stretching vibrations observed in the FT-IR spectra of these compounds discussed below.

In the ^{19}F NMR spectra of compounds **1**, **2**, **4**, and **5**, two doublets of the AA′XX′ spin system occur indicating a substitution of the aromatic ring at the C^4 carbon atom. The signal assigned to F^3 and F^5 atoms is found at higher

TABLE 4. ^{13}C NMR Chemical Shift (ppm) of Carbons of Aromatic Part and Coupling Constants (Hz) for Compounds 1−5

	^{13}C NMR data[a]					
compd	C^1	C^2	C^3	C^4	C^5	C^6
1	104.3 t $^2J_{CF} = 18.6$	145.4 m	142.1 m	129.6 t $^2J_{CF} = 11.4$	142.1 m	145.4 m
2	97.3 tt $^2J_{CF} = 19.5$ $^3J_{CF} = 2.0$	144.3 m	137.5 m	127.1 tt $^2J_{CF} = 11.5$ $^3J_{CF} = 2.3$	137.5 m	144.3 m
3	103.2 td $^2J_{CF} = {}^{2'}J_{CF} = 20.6$ $^3J_{CF} = 1.2$	142.8 ddd $^1J_{CF} = 242.2$ $^2J_{CF} = 13.7$ $^3J_{CF} = 2.8$	134.5 ddd $^1J_{CF} = 244.5$ $^2J_{CF} = 17.2$ $^4J_{CF} = 2.0$	121.1 dt $^2J_{CF} = 16.0$ $^3J_{CF} = {}^{3'}J_{CF} = 2.6$	117.6 ddd $^2J_{CF} = 14.0$ $^3J_{CF} = 6.9$ $^4J_{CF} = 2.6$	140.2 ddd $^1J_{CF} = 242.8$ $^3J_{CF} = 4.1$ $^4J_{CF} = 2.6$
4	97.8 tt $^2J_{CF} = 20.0$ $^3J_{CF} = 3.1$	144.5 m	135.9 m	126.9 tt $^2J_{CF} = 10.8$ $^3J_{CF} = 2.8$	135.9 m	144.5 m
5	98.0 tt $^2J_{CF} = 19.5$ $^3J_{CF} = 2.8$	144.5 m	137.6 m	126.8 tt $^2J_{CF} = 11.6$ $^3J_{CF} = 3.1$	137.6 m	144.5 m

[a] s, singlet; d, doublet; t, triplet; m, multiplet.

TABLE 5. ^{13}C NMR Chemical Shift (ppm) of Carbons of the Aliphatic Part and Coupling Constants (Hz) for Compounds 1−5[a]

	^{13}C NMR data								
compd	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}
1	52.9 t $^4J_{CF} = 2.8$	26.0	44.9	156.3	40.2	22.2	45.4	40.5 t $^4J_{CF} = 3.4$	
2	41.7 t $^4J_{CF} = 3.0$	27.8	44.3	156.8	45.6	21.9	47.6	35.5	
3	44.6 d $^4J_{CF} = 3.4$	28.8 or 28.9	47.4 or 47.5	162.1	44.7 d $^4J_{CF} = 4.0$	28.8 or 28.9	47.4 or 47.5		
4	41.5 t $^4J_{CF} = 4.6$	28.2	44.6	176.8	37.0	28.6	23.4	29.9	49.6
5	41.8 t $^4J_{CF} = 4.2$	27.6	47.3	175.8	30.7	17.9	39.2		

[a] d, doublet; t, triplet.

TABLE 6. ^{19}F NMR Chemical Shifts (ppm) and Coupling Constants (Hz) for Compounds 1−5

	^{19}F NMR data			
compd	F^2	F^3	F^5	F^6
1	−143.4 m $^3J_{FF} = 21.6$ Hz	−149.4 m $^3J_{FF} = 21.6$ Hz	−149.4 m $^3J_{FF} = 21.6$ Hz	−143.4 m $^3J_{FF} = 21.6$ Hz
2	−144.8 m $^3J_{FF} = 20.2$ Hz	−159.2 m $^3J_{FF} = 20.2$ Hz	−159.2 m $^3J_{FF} = 20.2$ Hz	−144.8 m $^3J_{FF} = 20.2$ Hz
3	−161.7 dd $^3J_{FF} = 21.4$ Hz; $^4J_{FF} = 13.2$ Hz	−145.7 dd $^3J_{FF} = 21.4$ Hz; $^5J_{FF} = 5.0$ Hz	-	−141.7 dd $^4J_{FF} = 13.2$ Hz; $^5J_{FF} = 5.0$ Hz
4	−144.9 d $^3J_{FF} = 18.4$ Hz	−159.5 m $^3J_{FF} = 18.4$ Hz	−159.5 m $^3J_{FF} = 18.4$ Hz	−144.9 d $^3J_{FF} = 18.4$ Hz
5	−144.3 m $^3J_{FF} = 23.8$ Hz	−159.2 m $^3J_{FF} = 23.8$ Hz	−159.2 m $^3J_{FF} = 23.8$ Hz	−144.3 m $^3J_{FF} = 23.8$ Hz

[a] d, doublet; m, multiplet.

fields due to the shielding effect of the C^4-N nitrogen atom, demonstrating that this amino group is bonded to C^4 atom.

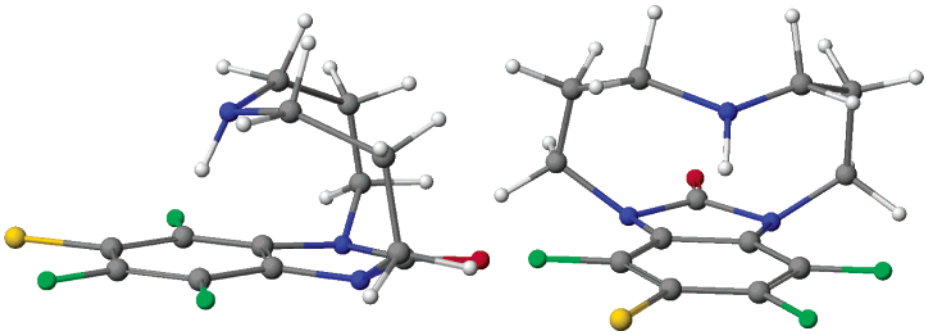
The ^{1}H, ^{13}C, and ^{19}F NMR spectra of compound **3** differ strongly from the corresponding spectra of the other compounds studied.

The fluorine spectrum of compound **3** shows three signals assigned to three nonequivalent nuclei. The coupling constants and chemical shifts of all these signals confirm a substitution of two nitrogen atoms at positions 4 and 5 at the aromatic ring.

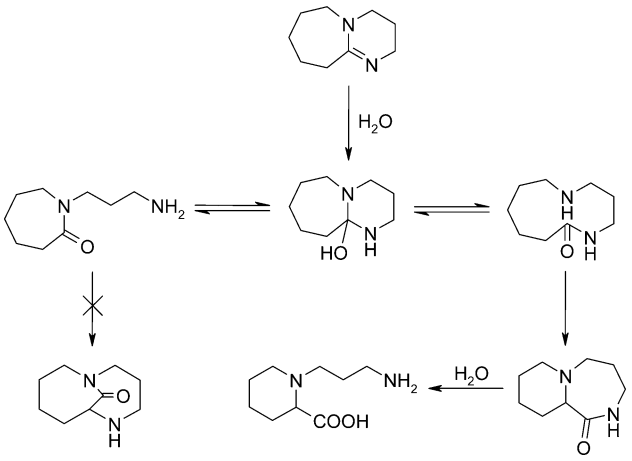
In ^{13}C NMR spectrum of compound **3**, the signals assigned to the pairs of C^7−C^{11} and C^8−C^{12} as well as C^9−C^{13} carbon atoms of methylene groups are found at comparable chemical shifts. A similar situation is also found in the ^{1}H NMR spectrum of this compound (Table 3). Furthermore, similar couplings between carbon atoms (C,^{7} C^{11}) of the aliphatic part and fluorine atoms (F^3, F^6) are observed (J = 3.4 Hz and J = 4.0 Hz, respectively). This result can be explained by the bonding of nitrogen atoms to the aromatic ring. The carbon atom of the urea group is also coupled with ^{19}F atoms and gives a strongly broadened signal at 162.10 ppm. All these results demonstrate the high symmetry of the aliphatic part of the compound **3**.

It is interesting to note that the NH signal in ^{1}H NMR

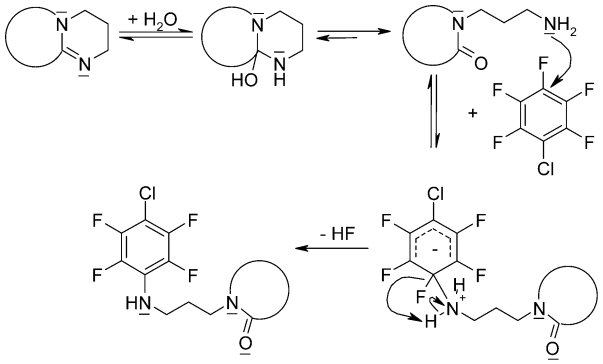
CHART 2. Structure of Compound 3 Calculated by the PM5 Method



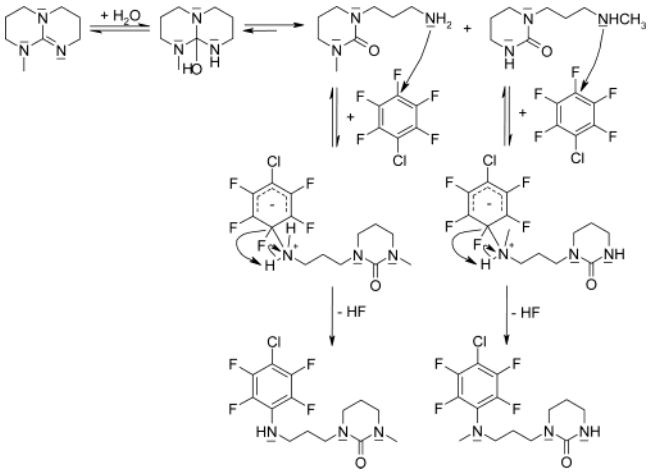
SCHEME 2. Reaction of DBU with Water



SCHEME 3. Mechanism of DBN or DBU with ClPFB Reaction



SCHEME 4. Mechanism of MTBD with ClPFB Reaction



spectrum of compound 3 is unexpectedly shifted to a very high field, which is a consequence of the interaction of this proton with the π electron system of the aromatic ring. This observation strongly supports the structure of compound **3** calculated by the PM5 semiempirical method as shown in Chart 2.

FT-IR Measurements. The most important bands observed in the spectra of compounds **1**−**5**, i.e., the ν-(N−H) and ν(C═O) stretching vibrations, are collected in Table 2. The wavenumbers at which these bands occur are typical of substituted lactams with 5−7-membered rings in the solid state.[28] A typical lactam structure is observed only in compound **1** and due to this reason the three N−H stretching vibrations are observed in its spectrum at 3293, 3218, and 3063 cm^{-1} indicating its dimerization in the solid state. The lactam **1** has a cis configuration in respect to the amide group and, therefore, no amide II band at about 1550 cm^{-1} is found in the spectrum. The same is observed in the spectra of all other compounds because of the substitution of the lactam N-atoms. The structure of compound **3** can be described as that of an N-substituted derivative of benzimidazole. The ν(C═O) stretching vibrations in the spectra of such compounds arise at higher wavenumbers at about 1720 $cm^{-1}$and have been extensively studied in the literature.[29]

The Mechanism of the Reaction. It is known from literature that the hydrolysis of DBU proceeds in two slow steps. First, the hydroxyl derivative as an intermediate product is formed, and finally, substituted *N*-(3-aminopropyl)caprolactam together with *N*-(3-aminopropyl)-2-piperidinecarboxylic acid is observed (Scheme 2) with the yield of the lactam being predominant.[30]

Taking this result into account, we can conclude that the observed products (compounds **1**−**5**) are formed in the reaction of the respective aminolactams with chloropentafluorobenzene via Meisenheimer complexes. This mechanism of the reactions with various N-bases is shown in Schemes 3−5.

The mechanism proposed is supported by the following observations: (1) No reaction, especially no formation of

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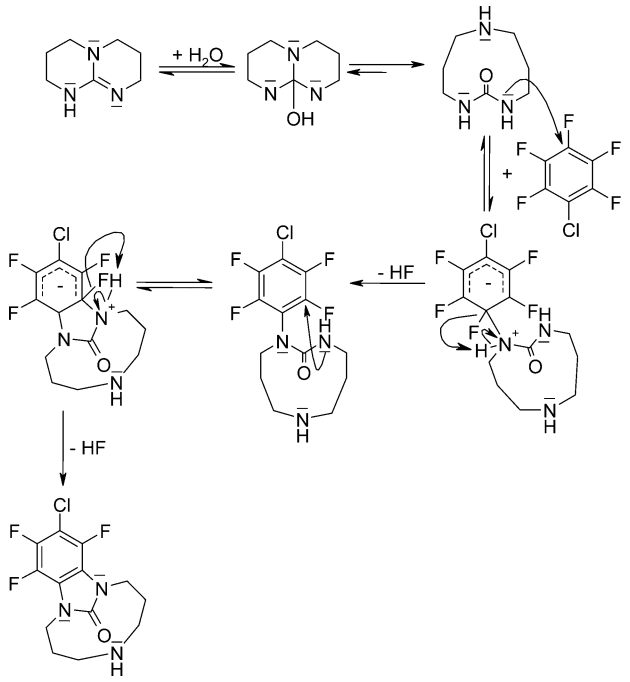
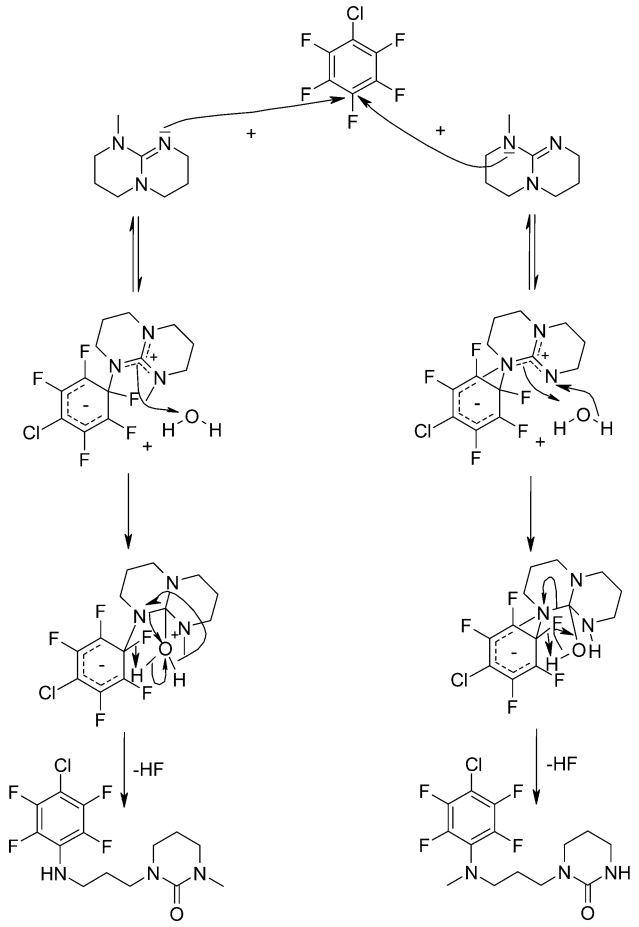
(30) Patai, S.; Rappoport, Z. *The Chemistry of Amidines and Imidiates*; John Wiley and Sons: Chichester, 1991; p 782.

SCHEME 5. Mechanism of TBD with ClPFB Reaction



SCHEME 6. Alternative Mechanism of MTBD with ClPFB Reaction



Meisenheimer complexes can be detected by spectroscopic methods if chloropentafluorobenzene and strong N-bases are mixed without water molecules. (2) A nucleophilic attack of N-CH_3 and N nitrogen atoms of MTBD molecule on the carbon atom at position 4 (Scheme 6) is unlikely also due to the stereochemical reasons, whereas the formation of both aminopropylpiperimidones after hydrolyses of MTBD is highly probable (Scheme 4). (3) The N-bases studied exhibit high basicity but relatively low nucleophilicity.[4−7,31−35] (4) The kinetic data of the hydrolyses of DBN and the mixture of DBN with chloropentafluorobenzene are comparable. Thus, the rate-determining step of these reactions is the hydrolysis of the N-base.

In the case of TBD with a water molecule, the formation of 1,3,7-triaza-2-oxodecane can occur, which condenses with chloropentafluorobenzene to benzimidazole derivative with elimination of two HF molecules (Scheme 5).

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