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Effect of N-substituents on protonation chemistry of trichlorophosphazenes

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Abstract

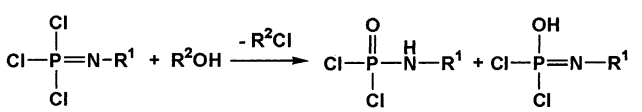
The protonation chemistry of trichlorophosphazene (R^1–N=PCl_3) with sulfonic acids (R^2SO_3H) was found to be affected by the N-substituents R^1, yielding bis(sulfonyl)imides containing both R^1 and R^2, and mixed sulfonylphosphonyl imides containing either R^1 or R^2. In the formation of the latter a hitherto unobserved chemistry occurred. An intramolecular 'imine SN_2' mechanism was proposed to rationalize the reactions observed.

Keywords: Protonation chemistry; Trichlorophosphazenes; Bis(sulfonyl)imides

1. Introduction

The first member of the trichlorophosphazene family, trichlorophosphazosulfonyl chloride, $ClSO_2N$=PCl_3, was made by Ephraim and Gurewitsch [1], but it was mistakenly identified as the adduct of NH_2SO_2Cl and PCl_3. Not until four decades later did Kirsanov [2] correct the error and embark on a three decade period of fruitful research on phosphazene chemistry, during which a large number of P- or N-substituted phosphazenes were synthesized [3–9]. Much effort has been made to understand the toxicology of these due to their importance as microbiocides [3–11]. Extensive knowledge of their structure and physical properties was also obtained using a variety of spectroscopic means including IR [12], ^{31}P, ^{15}N and ^{35}Cl NMR [13,14], photoelectron spectrum [15] and dielectric studies [16] as well as molecular orbital computation approaches [17].

The understanding of the phosphazene chemistry included cyclo-dimerization [4,7,18,19], hydrolysis [18,20,21], solvolysis with protic solvents like alcohols and phenols [22,23], and acidolysis with almost exclusively carboxylic acids, especially formic acid [24–26]. With those weak proton-donors the protonation chemistry was exhaustively investigated using almost every known member of the phosphazene family, and it was found that all of the protonation reactions conform to a so-called 'chlorine–oxygen exchange' rule [22], where the phosphorus dechlorinates and acquires oxygen, leaving imidic nitrogen protonated as shown in Eq. (1).



R^1 = alkyl, phenyl, acyl, alkylsulfonyl or phenylsulfonyl;
R^2 = alkyl, phenyl or acyl

(1)

Between the two protonated products shown in Eq. (1), the O-protonated tautomer (phosphoric acid) was found to be disfavored in the equilibrium with the N-protonated tautomer (imidic acid) in most cases, while phosphazenes with not so electron-deficient phosphorus centers, e.g. certain substituted $Cl_nR^2_{3-n}P$=N–R^1 [24] (R^1 = alkyl or acyl, R^2 = alkyl or phenoxide; $n = 1$–2), yield the O-protonated tautomer as the dominant species.

The only known exception to the 'chlorine–oxygen exchange' rule was found in the acidolysis of trichlorophosphazene with acids stronger than car-

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boxylic acids, where P=N bond cleaves followed by the formation of a bis(sulfonyl)imides [27–29] as shown in Eq. (2):

$$\begin{matrix} HSO_3Cl \\ \text{or} \\ HSO_3F \end{matrix} + Cl_3P{=}NSO_2Cl \xrightarrow{-POCl_3} \begin{matrix} HN(SO_2Cl)_2 \\ \text{or} \\ FSO_2NHSO_2Cl \end{matrix} \quad (2)$$

This exception to 'chlorine–oxygen exchange' reaction presents a potentially valuable route to the synthesis of bis(sulfonyl)imide, which has been a challenge because it is usually difficult to introduce the second sulfonyl group onto the already non-nucleophilic sulfamide nitrogen center[1] [30]. For example, a well-known synthesis of bis(sulfonyl)imide involved laborious combination of N-deprotonation/silylation as means of activating the nucleophilicity of nitrogen center, and subsequent Si–F bond formation as additional driving force, leading to a series of bis(perfluoroalkylsulfonyl) imidic acids [31,32]. This procedure is far more complicated compared with the acidolysis of phosphazene (Eq. (2)), in which the tricholorophospho moiety acts as activating agent, and relatively mild sulfonic acids are used instead of their corresponding acid halides. However, to the best of our knowledge, no serious effort has been made to explore the possibility of applying the chemistry in Eq. (2) to the synthesis of bis(sulfonyl)imides, following the first reports by Appel et al. [28] and Ruff [30].

In recent years, lithium salts based on bis(sulfonyl)imide anions have been given much attention due to the discovery of their promising properties as electrolyte solutes [33]. Because of the large anion size and low melting point, this class of lithium salts has high solubility and ion conductivity in non-aqueous solvents. It is the interest of this research group in seeking new low melting, stable lithium salts [34–37] that has led us to explore an economical synthetic route to imide anions with unsymmetrical structure. A serendipitous result of this synthetic endeavor is the further understanding about the little-known protonation chemistry of phosphazenes, which we report in this paper.

2. Experimental

All sulfonic acids were obtained from commercial sources. All solvents were distilled before use, while other chemicals were used as received. All the synthetic procedures were carried out under the protection of N_2 from a vacuum manifold. Trichlorophosphazenes with general formula of $R^1N{=}PCl_3$ were prepared according to Kirsanov with or without solvents [2,3]. Protonation was conducted by adding sulfonic acids to trichlorophosphazenes with vigorous stirring. Some protonation reactions were very exothermic and the reaction mixture required cooling, using salt/ice bath. Other protonations proceeded so sluggishly that heating was required for the reaction to reach completion. In all cases a cold trap cooled by acetone/dry ice was connected to the reaction vessel so that the volatile products could be collected and subjected to analysis. The imidic acids were then fractionated under vacuum (between 0.1 and 5 mmHg) and collected at 1–2°C boiling range (boiling points were not corrected). Recrystallization in appropriate solvents was conducted when the protonated products were solid at room temperature, and the melting points were determined using differential scanning calorimetry (Perkin–Elmer DSC-7).

For the liquid imidic acids the elemental analysis was conducted on their lithium salts, which were made either by metathesis with LiCl or by neutralization with LiH, followed by purification through recrystallization from appropriate solvents.

^1H and ^{13}C NMR spectra, using $Si(CH_3)_4$ as internal reference, were collected on a Varian Gemini 300, while ^{31}P and ^{19}F NMR spectra with 85% H_3PO_4 as external reference and $CFCl_3$ as internal reference, respectively, were obtained with an Oxford 400. IR spectra were recorded with a Galaxy Series FT-IR model 2020 using liquid film on KBr despite the fact that most of the synthesized imidic acids react with KBr, rendering it difficult to observe the characteristic N–H vibration. Mass spectra (EI, Source temp. 250°C) were carried out with a Finnigan MAT Model 312 using either ether or acetone as carrier.

3. Results

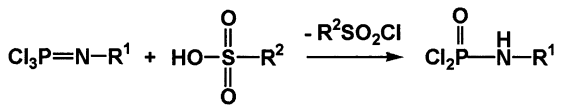
The acidolysis of phosphazene with sulfonic acids was found to strongly depend on N-substituent R^1. Among the substituents studied in this work, the protonation reaction can be classified into three distinct categories as summarized by Tables 1–3, in which the major structural identification data of the protonated products are also listed along with the synthesis and physical properties.

(1) R^1 is alkyl, where 'chlorine–oxygen exchange' is observed as shown by Eq. (3) in Table 1. The main backbone of the molecule R^1–N=P remains intact while N is protonated and P-oxygenated.

Fig. 1 shows the ^{31}P NMR spectra of CH_3–N=PCl_3 (a) and its protonated product CH_3–N(H)P(O)Cl_2 (b). It has been known that when R^1 is alkyl, trichlorophos-

[1] The basicity of nitrogen is much reduced by the strongly electron-withdrawing sulfonyl group, e.g. compare $pK_a = 3.8$ for R–NH–SO_2R′ with $pK_a = 20–30$ for R–NH–R′ in aqueous media.

Table 1
R^1 = alkyl [a]: 'chlorine–oxygen exchange' rule



(3)

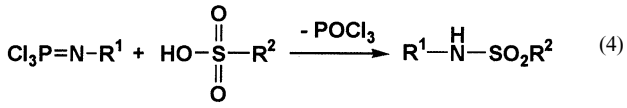
R^1	R^2	B.p. (°C/mmHg)	Yield (%) [b]	NMR (ppm, $CDCl_3$)			Major m/z [c]
				^1H	^{13}C	^{31}P	
CH_3	Cl	98/5	38	2.82 (d, $J_{P(H}$ 19.80 Hz, 3H), 5.75 (br, 1H)	28.23 (s)	19.60 (q, $J_{P(H}$ 19.80 Hz)	147 (M^+), 131 ($NPOCl_2^+$) 117 ($POCl_2^+$), 101 (PCl_2^+), 83 ($POHCl^+$), 66 (PCl^+)
CH_3	CF_3	140/10	81	2.80 (d, $J_{P(H}$ 19.80 Hz, 3H), 5.69 (br, 1H)	28.23 (s)	19.61 (q, $J_{P(H}$ 19.80 Hz)	
CH_3CH_2	CH_3	110/3	73	0.96 (t, 3H), 3.04 (m, 2H), 5.40 (br, 1H)	28.22 (s)	19.58 (q, $J_{P(H}$ 20.11 Hz)	161 (M^+), 117 ($POCl_2^+$), 101 (PCl_2^+), 83 ($POHCl^+$), 66 (PCl^+), 44 ($C_2H_5NH^+$)

[a] The phosphazenes are in the form of dimer $(Cl_3P–NR^1)_2$ as confirmed by their ^{31}P NMR spectra. For example, in spectra for $(Cl_3P–NCH_3)_2$ a heptet (δ −78.30 ppm, $J_{P–H}$ 21.30 Hz) was observed due to the P–H coupling with protons on two neighboring methyl groups.

[b] Isolated yields.

[c] Only the first 4–6 peaks in the relative abundance order are shown.

Table 2
R^1 = alkyl- or halosulfonyl: formation of bis(sulfonyl)imides



(4)

R^1	R^2	B.p. (°C/mmHg)	Yield (%)	NMR (ppm, $CDCl_3$ or acetone-d_6)			Major m/z
				^1H	^{13}C	^{19}F	
$ClSO_2$	F	115/2.0 [a]	70	9.88 (br)		58.56 (s)	197 (M^+), 162 ($FSO_2NHSO_2^+$), 113 ($ClSO_2N^+$), 99 ($ClSO_2^+$), 83 (SO_2F^+)
$ClSO_2$	Cl	95/1.0 [b]	88	9.83 (br)			213 (M^+), 178 (Cl $SO_2NHSO_2^+$), 113 ($ClSO_2N^+$), 99 ($ClSO_2^+$)
$ClSO_2$	CF_3	110/8.0	72	11.25 (br)	118.38 (q, J_{C-F} 317.20 Hz)	73.50 (s)	247 (M^+), 211 ($CF_3SO_2NSO_2^+$), 177 ($ClSO_2NSO_2^+$) 147 ($CF_3SO_2N^+$), 133 ($CF_3SO_2^+$), 69 (CF_3^+)
CH_3SO_2	CF_3	87/0.5	60	3.70 (s, 3H), 11.2 (br, 1H)	48.76 (s), 114.68 (q, J_{C-F} 317.20 Hz)	74.20 (s)	227 (M^+), 212 ($CF_3SO_2NHSO_2^+$), 157 ($CH_3SO_2NSO_2^+$), 147 ($CF_3SO_2N^+$), 93 ($CH_3SO_2N^+$), 69 (CF_3^+)
$C_6H_5SO_2$	CF_3	85/0.1	39	7.5 (m, 3H), 7.7 (m, 2H), 11.67 (br, 1H)	48.70 (s), 114.71 (q, J_{C-F} 318.30 Hz), 123.2 (s), 126.19 (s), 132.04 (s), 140.36 (s)	70.12 (s)	289 (M^+), 155 ($C_6H_5SO_2N^+$), 77 ($C_6H_5^+$), 69 (CF_3^+)
$C_6H_5SO_2$	CH_3	150(dec.)	~30 [c]	7.4 (m, 3H), 3.68 (s, 3H), 7.7 (m, 2H), 8.67 (br, 1H)	37.66 (s), 123.88 (q, J_{C-F} 318.30 Hz), 125.1 (s), 130.2 (s), 136.1 (s)		155 ($C_6H_5SO_2N^+$), 141 ($C_6H_5SO_2^+$), 93 ($CH_3SO_2N^+$), 79 ($CH_3SO_2^+$), 14 (CH_2^+)

[a] White needle with m.p. 15.5°C.
[b] White needle with m.p. 35.5°C.
[c] The attempt to isolate this acid failed due to the decomposition upon distillation and the difficulty associated with recrystallization. The listed yield was estimated from that of the isolated Li-salt. The instability of the acid is also reflected in the absence of M^+ in its mass spectra.

Table 3
R^1 = trifluoroacyl [a]: a new protonation chemistry with the formation of mixed sulfonylphosphonyl imides

(5)

R^1	R^2	B.p. (°C mm^{-1})	Yield (%)	NMR (ppm, $CDCl_3$)			Major *m/z*
				^1H	^{13}C	^{31}P	
CF_3CO	CF_3	150/20	73 [b]	9.45 (br)	116.91 (q, J_{C-F} 317.17 Hz)	15.22 (s)	265 (M^+), 147 ($CF_3SO_2N^+$), 131 ($NPOCl_2^+$) 117 ($POCl_2^+$), 101 (PCl_2^+), 83 ($POHCl^+$), 69 (CF_3^+), 66 (PCl^+)
CF_3CO	CH_3	120/3	95 [b]	3.43 (s, 3H), 10.50 (br, 1′H)	41.41 (s)	7.39 (d, J_{P-H} 6.153 Hz)	211 (M^+), 117 ($POCl_2^+$), 101 (PCl_2^+),93 ($CH_3SO_2N^+$), 82 ($POCl^+$), 79 ($CH_3SO_2^+$), 66 (PCl^+)
CF_3SO_2	CH_3	96/1.0	76 [b]	3.36 (s, 3H), 10.46 (br, 1′H)	41.45 (s)	7.35 (d, J_{P-H} 6.168 Hz)	211 (M^+), 117 ($POCl_2^+$), 101 (PCl_2^+), 93 ($CH_3SO_2N^+$), 66 (PCl^+)

[a] The gaseous products (R^1Cl) were trapped at −78°C and then subject to analysis. In all cases positive identification of R^1Cl was obtained by ^{13}C NMR; for analytic and measurement conditions see footnote of Table 1.
[b] White needle with m.p. 55.5–56°C.

phazenes tend to dimerize [4,7,18,19], forming a dative bond between the electron-rich center N and electron-deficient center P, as shown by the structure in Fig. 1(a). The dimeric structure has been supported by molecular weight measurement by ebullioscopy [7], while the heptet P signal observed in the P–H coupling experiment (inset of Fig. 1(a)) is a more direct evidence confirming the four member-ring structure of this molecule, i.e. each P nucleus is split by two neighboring methyl groups instead of one as in a monomer. On the other hand, the protonated compound, with a reduced electron donicity on N, is shown to be an apparent monomer (inset of Fig. 1(b)), where only one methyl is adjacent to the P nucleus.

(2) R^1 is sulfonyl, where bis(sulfonyl)imides are formed as shown by Eq. (4) in Table 2. During the reaction, R^1–N remains unchanged but the P-containing moiety is replaced by the sulfonyl group bearing R^2. We think that reactions in this category deserve to be exploited as simple synthetic routes to new imidic acids, with yields ranging from fair to good.

(3) R^1 is acyl, where a hitherto unobserved reaction occurs with the formation of a mixed sulfonylphosphonyl imide, as shown by Eq. (5) above Table 3. The process is a reversal of Eq. (3) above Table 1, i.e. R^1 is replaced by sulfonyl group bearing R^2 while the P-containing moiety is oxygenated.

4. Discussion

4.1. Protonation mechanism: weak acids

The Kirsanovian rule of protonation has been strictly followed when the proton donor is a weak acid [18,20–23], as shown in Eq. (1). Although this type of reaction has been systematically studied, there has not been any attempt to rationalize its possible mechanism.

Considering the much reduced basicity of N in trichlorophosphazenes compared with ordinary amine nitrogens, we believe that, instead of direct proton addition to N, more likely the solvolysis/acidolysis with weak proton donors (e.g. alcohol or carboxylic acids) starts with an initial nucleophilic attack by oxygen in the proton donor on the electrophilic P, which is then followed by protonation on N:

R^1 = alkyl, alkylsulfonyl or arylsulfonyl,
R^2 = alkyl, aryl or acyl (6)

In other words, the actual *protonating agent* is HCl, no matter what *protic agent* (acid) is used. This seems

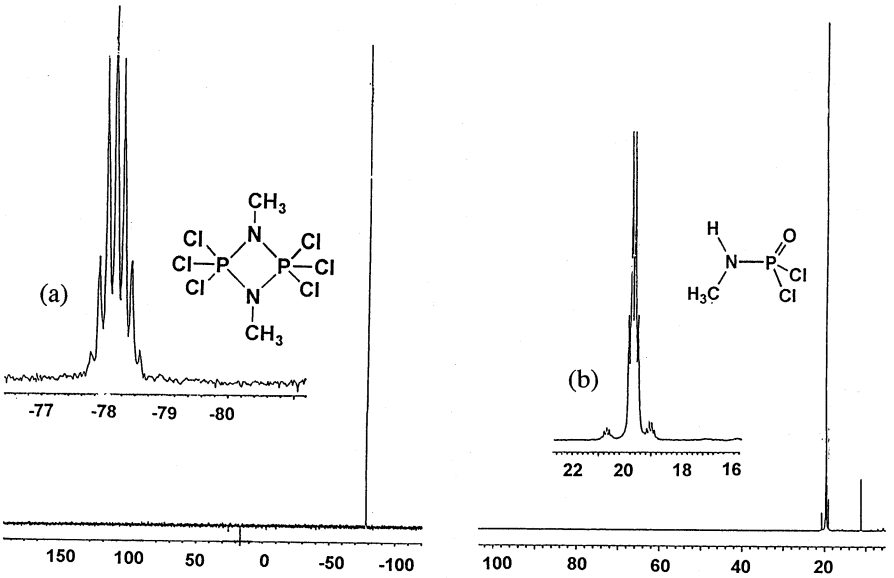


Fig. 1. ^{31}P NMR spectra for CH_3–N=PCl_3 (a) and its protonated product CH_3–N(H)P(O)Cl_2 (b). Inset: ^{31}P multiplicity with P–H coupling.

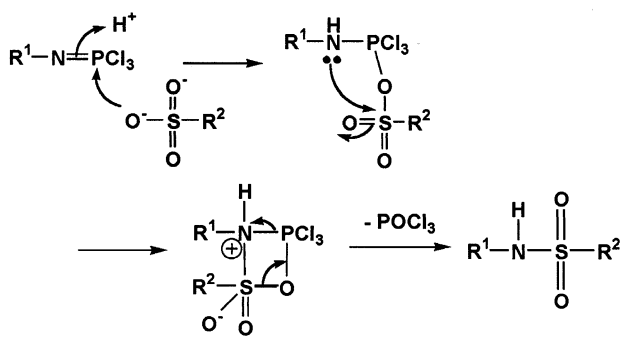
reasonable because, irrespective of the protic agent used, the structure of the protonated product remains the same.

The above two step hypothesis was supported by the observation that, while treatment of CH_3–N=PCl_3 with PhONa readily afforded nucleophilic substitution product triester, CH_3–N=$P(OPh)_3$, only protic agent PhOH can lead to protonated product CH_3–NH–$POCl_2$ [23]. More convincing evidence is that, even when a protic agent was present, if HCl produced from the initial nucleophilic attack was rapidly removed from the reaction medium, the protonation would not occur [38]. Thus, the proposed mechanism seems to hold true for the protonation chemistry of trichlorophosphazenes with weak proton donating agents (weak Brønsted acids).

4.2. Protonation mechanism: strong acids

However, when the proton source is a strong protonating agent (strong acid), the rule no longer holds true in all the cases but depends on the N-substituents as we have shown in Eqs. (2)–(5), i.e. only when R^1 is alkyl, is the Kirsanovian type of reaction observed (Eq. (3)). Obviously, the change is caused by the higher protonating strength of the sulfonic acids compared with alcohols, phenols and carboxylic acids.

For sulfonic acids, the much lower O-donicity makes it a dubious nucleophile for the electron-deficient P-center; rather, the strongly acidic proton tends to function as a specific proton catalyst. Furthermore, this protonation of N would in turn increase the electrophilicity of P, thus assisting an O-attack from the sulfonate anion (step 1 in Eq. (7)). The resultant intermediate (which could be considered a transition state in a more concerted mechanism) would undergo an intra-molecular SN_2 process, resulting in the formation of a new S–N bond. The neutral, stable species $POCl_3$, is eliminated in a subsequent rearrangement resulting in the desired bis(sulfonyl)imide (step 2 and 3 in Eq. (7)).



(7)

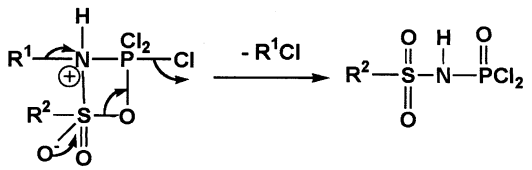
Apparently, the crucial factor governing the key step in the formation of the new S–N bond is the N-nucleophilicity. It is a logical inference that, in the hypothetical intermediate amide, the N-nucleophilicity is higher than in either starting agent R^1–N=PCl_3 or the intermediate imine in Eq. (6), in which case the above-proposed intramolecular 'imine SN_2' reaction mechanism seems reasonable based on current knowledge about N-basicity [39].

Compared with the mechanism for weak acid protonation (Eq. (6)), the chemistry in Eq. (7) with strong acids represents 'specific proton catalysis' by the sulfonic acids used, i.e. the *protonating agent* here is the *protic agent* itself. As would be expected the protonated product bears the structural signature (R^2–SO_2) of the protic agents (Table 2).

4.3. Effect of N-substituent R^1 on protonation mechanism

It should be pointed out that the four-member cyclic ammonium intermediate in Eq. (7) is only hypothetical. In reality the formation of the final product bis(sulfonyl)imide could have involved anything between a multi-step process with distinctive intermediates and a complete concerted one step process.

On the other hand, if such an intermediate does exist, then indirect evidence for such a 'proton catalysis' rationale would be the formation of an N-sulfonation product other than the products observed in either of Eqs. (3) and (4), i.e. a third possibility which will produce an R^2-containing mixed phosphonylsulfonylimide, as follows in Eq (8):



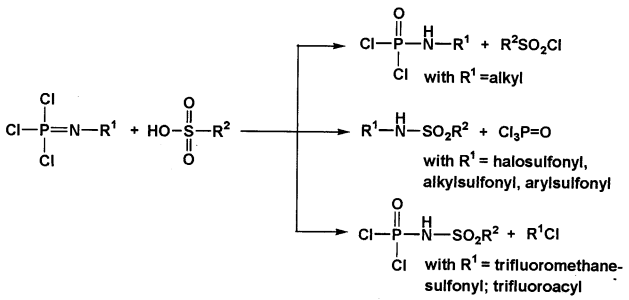
(8)

This is actually observed in Eq. (5) (Table 3), when R^1 is a very good leaving group, e.g. as trifluoromethanesulfonyl ($CF_3SO_2^-$) and trifluoroacyl (CF_3CO^-), and the R^1-moiety can be readily removed. To the best of our knowledge this phosphazene-protonation chemistry has not been reported before. Note the last two entries of Table 3, where the protonation of different phosphazenes with the same acid CH_3SO_3H results in identical protonated products. This should be viewed as strong evidence that all the protonation proceeds via a common intermediate as suggested in Eq. (7).

The situation with R^1 being alkyl is the most interesting. The high N-basicity and P-(Lewis) acidity in this class of phosphazene, which can be seen in the split pattern of P–H coupling of the ^{31}P resonance in Fig. 1(a), is the reason that cyclic dimerization occurs. The protonation chemistry of the dimer, when being treated with sulfonic acids, proceed according to Eq. (6) instead of Eq. (7), probably either due to electronic factor, i.e. an electron availability of N being stripped by bridging P-centers, or a steric factor, i.e. sulfonate anion attack on P is more facile than N-protonation.

5. Conclusion

It has been discovered that the protonation chemistry of trichlorophosphazenes with strong acids is distinctively different from that with weak acids. In sharp contrast with the simplicity of the latter case, protonation chemistry with strong acids depends on N-substituents R^1, and with R^1 being trifluoromethanesulfonyl or trifluoroacyl, a hitherto unobserved reaction occurs. The above chemistry can be summarized in the following Scheme:



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