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Paper

Brønsted and Lewis acid adducts of triazenes

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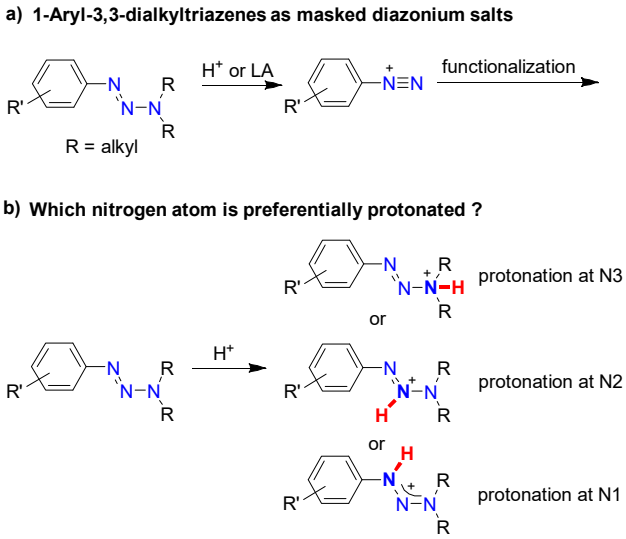
The synthetic utility of triazenes rests on the fact that the triazene function can be cleaved by Brønsted or Lewis acids, liberating diazonium compounds. However, the preferred coordination site of the acid is still a matter of debate. We have analyzed triflic acid, $B(C_6F_5)_3$, and $PdCl_2$ adducts of triazenes by NMR spectroscopy and single crystal X-ray crystallography. In all cases, we observe coordination of the acid to the N1 atom of the triazene. This finding is not only of relevance for acid-induced cleavage reactions, but also for metal-catalyzed reactions with triazenes, which are increasingly being used in synthetic organic chemistry.

Introduction

Aryl diazonium salts are versatile reagents in synthetic organic chemistry.[1] However, handling and isolation of these sensitive compounds can be problematic.[2] 1-Aryl-3,3-dialkyl triazenes represent surrogates for aryl diazonium compounds.[3] These triazenes are easily accessible, and they are stable under neutral or basic conditions. The addition of Brønsted or Lewis acids results in cleavage of the triazene group and liberation of an aryl diazonium compound, which can then engage in further functionalization (Scheme 1a).[3]

The mechanism of the acid-induced cleavage of triazenes has been studied extensively, both experimentally (kinetic studies),[4,5] and theoretically.[6] These studies were not only motivated by the synthetic utility of triazenes, but also by the fact that triazenes can display biological activity.[7] A recurring topic is the question of which nitrogen atom is preferentially protonated upon addition of acid (Scheme 1b). In the case of 1-aryl-3,3-dialkyl triazenes, the N3-protonated compound is often depicted as the intermediate.[3b,8] N3 protonation is expected to weaken the N2–N3 bond, thereby promoting the formation of the diazonium compound. However, computational analyses indicate that N1 is equally or even more basic than N3.[6,9] It is worth noting that an N1-protonated triazene would benefit from charge delocalization. However, such delocalization is expected to strengthen the N2–N3 bond, in contrast to the experimentally observed reactivity (cleavage of the N2–N3 bond). Indirect evidence for the relevance of an N1-protontated triazene was presented by Pytela and co-workers.[5b] From studying the kinetics of the reaction of 3-alkyl-1,3-diaryl triazenes with trichloroacetic acid in hexane, they concluded that a 'non-reactive associate' is formed between two molecules of trichloroacetic acid and the N1 atom of the triazene. The structure of this hypothetical trimer was not specified, but a polar associate was favored over an ion pair.



Scheme 1. Brønsted or Lewis acid-induced conversion of 1-aryl-3,3-dialkyltriazenes into diazonium compounds (a), and the question of the relative proton affinity of the N atoms.

Over the last five years, our group has studied the chemistry of triazenes, with special focus on triazenes with unusual alkynyl,[10] alkenyl,[11] allenyl,[12] and acyl substituents.[13] During the course of these investigations, we realized that protonated triazenes might be sufficiently stable for a direct characterization at low temperature. This hypothesis could be confirmed, and we were able to obtain structural and spectroscopic data for these elusive intermediates. Encouraged by these results, we have also investigated the interaction of triazenes with Lewis acids. The results of our study are summarized below.

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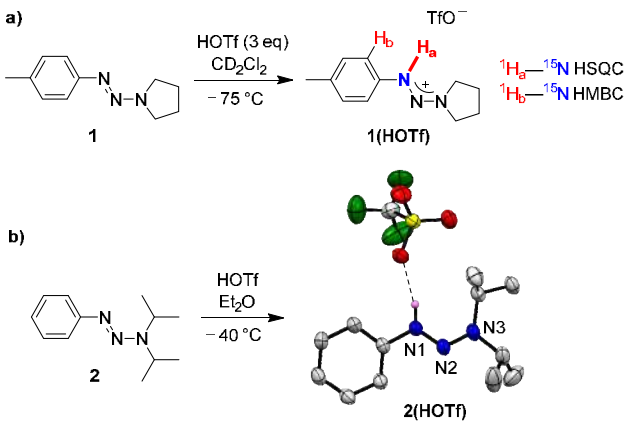
Results and discussion

Brønsted acid adducts of triazenes

A mixture of triazene **1** (Scheme 2a) and triflic acid (HOTf) in dichloromethane was found to be stable for prolonged periods of time at temperatures below –5 °C, providing the opportunity to perform low-temperature NMR studies. To elucidate the interaction of HOTf with the triazene, we have recorded HSQC and HMBC NMR spectra at –75 °C for determining ^{1}H-^{15}N and ^{1}H-^{15}C correlations (for details, see the ESI). The addition of HOTf resulted in the appearance of a ^{1}H NMR signal at 11.98 ppm, which we attribute to the newly formed NH proton. The identity of the ^{15}N NMR signal of N1 was revealed by a ^{1}H-^{15}N HMBC spectrum, which showed a cross peak between the ^{1}H NMR signal of the aromatic proton H_b at 7.41 ppm and a ^{15}N NMR signal at 200 ppm. A cross peak in the ^{1}H-^{15}N HSQC spectrum indicated that the proton giving rise to the signal at 11.98 ppm is directly bonded to the N1 atom with the signal at 200 ppm. Additional confirmation was obtained by a ^{1}H-^{15}C HMBC spectrum, which showed cross peaks between the ^{1}H NMR signal at 11.98 ppm and ^{13}C NMR signals of aromatic carbon atoms. Taken together, the data provide clear evidence for the selective formation of an N1-protonated triazene, **1(HOTf)**.



Scheme 2. Protonation of the aryl triazenes **1** (a) and **2** (b), and molecular structure of **2(HOTf)** in the crystal. The thermal ellipsoids are at 50% probability. With the exception of NH, hydrogen atoms are not shown for clarity.

Eager to complement our solution-based analysis with structural data, we have performed low temperature crystallizations of different aryl triazene/HOTf/solvent mixtures. Suitable single crystals were finally obtained for aryl triazene **2**, using diethyl ether as solvent. A crystallographic analysis confirmed that the proton is located at N1 position (Scheme 2b, Table 1). It is worth noting that the hydrogen atom bound to nitrogen was found in a difference map and refined freely.

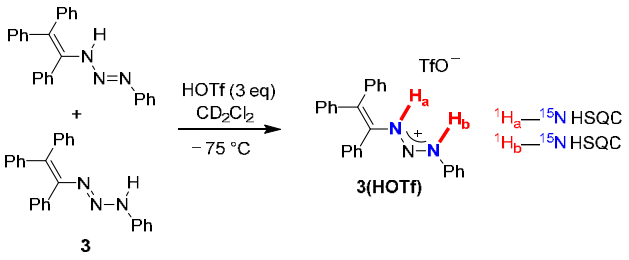
In line with the anticipated charge delocalization, the N2–N3 bond of **2(HOTf)** (1.284(2) Å) has a similar length than the N1–N2 bond (1.294(3) Å). For comparison, we have analyzed 30 structures of neutral 1-aryl-3,3-dialkyl triazenes found in the CCDC database (for details, see the ESI). The average bond length observed for N1–N2 is 1.28 Å, and the average N2–N3 bond length is 1.33 Å. The most pronounced effect of protonation is thus a shortening of the N2–N3 distance. The plane defined by the three nitrogen atoms of **2(HOTf)** is nearly coplanar with the plane of the phenyl ring. One oxygen atom of the triflate anion is found within hydrogen bonding distance to the N-H group (N1···O1 = 2.859(3) Å).

Table 1. Selected bond lengths (Å) and angles (°) for the triazene adducts described in this manuscript.

Comp.	N1–N2	N2–N3	∠N1N2N3	N-B/Pd
2(HOTf)	1.294(3)	1.284(2)	119.29(19)	/
5(HOTf)	1.310(2)	1.265(2)	120.07(13)	/
6(HOTf)	1.319(2)	1.256(2)	121.18(17)	/
8	1.303(3)	1.278(3)	126.5(2)	1.618(3)
9	1.293(3)	1.288(3)	124.1(2)	1.615(3)
10	1.282(12)	1.267(11)	122.6(8)	2.045(7)
	1.286(12)	1.266(11)	122.5(8)	2.046(7)
11	1.304(3)	1.270(3)	123.6(2)	2.018(2)

Having established that aryl triazenes are preferentially protonated at the N1 position, we next investigated the protonation of vinyl triazene **3** (Scheme 3). Compound **3** is of synthetic value, because it can be used for the C-H vinylation of aromatic compounds.[11a] The resulting aryltriphenylethenes are of interest because of their aggregation-induced emission properties.

Triazene **3** crystallizes as a mixture of two tautomers,[11a] the structures of which are depicted in Scheme 3. The low temperature ^{1}H NMR spectrum of **3** (CD_2Cl_2, –75 °C) shows two NH signals at 9.73 and 9.66 ppm (ratio: ca. 2:1), which likely correspond to the two tautomeric forms. Upon addition of HOTf, one can observe two new NH signals of equal intensity at 11.82 and 11.64 ppm. The ^{1}H-^{15}N HSQC spectrum shows cross peaks to ^{15}N NMR signals at 201.5 and 214.9 ppm, which can be attributed to N1 and N3. The data suggest that both tautomers of **3** were protonated at N1 position, thereby converging to the same resonance-stabilized structure **3(HOTf)**.



Scheme 3. Protonation of vinyl triazenes **3**.

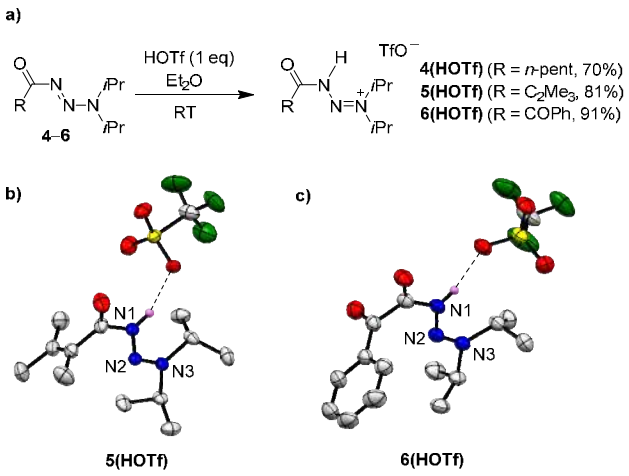
Finally, we have studied the protonation of 1-acyl triazenes (**4**–**6**, Scheme 4).[13] The presence of an acyl group at N1 position was expected to lower the proton affinity of this site. In

addition, the oxygen atom of the acyl group represents a new potential protonation site.[14]

First test experiments revealed that protonated 1-acyl triazenes are more stable than protonated 1-aryl-3,3-dialkyl triazenes. We were thus able to obtain the triflic acid salts on a preparative scale. The addition of triflic acid to a solution of the triazenes in diethyl ether led to the immediate formation of precipitates, which were isolated in yields between 70 and 91% (Scheme 4a). All three solids were found to be stable when stored under N_2 atmosphere at –40 °C. Analyses of the powders by IR spectroscopy showed bands at 1765–1743 cm^{-1} for the carbonyl groups. In addition, we observed new absorptions at 1579–1545 cm^{-1} for all three compounds. This value corresponds to what is expected for an amide II-type band. The IR spectra were therefore first indirect evidence that protonation had also occurred at N1 position.

The salts **5(HOTf)** and **6(HOTf)** were crystallized by using layering techniques at low temperature (see ESI). Crystallographic analyses revealed that in both cases, protonation had occurred at N1 position (Scheme 4b and 4c; the H atoms bound to N1 were found in a difference map and refined freely). Instead of balanced N1–N2 and N2–N3 bond distances, as observed for **2(HOTf)**, we find shorter N2–N3 bonds and longer N1–N2 bonds for **5(HOTf)** and **6(HOTf)** (Table 1). The electronic situation in these compounds is therefore best described with a mesomeric form showing a double bond between N2 and N3 (Scheme 4a). As in the case of **2(HOTf)**, one can observe hydrogen bonds between the triflate anion and the N-H group of the cation. For **5(HOTf)**, the triflate anion links two adjacent cations via hydrogen bonds (N1···O4 = 2.831(2) and 2.919(2) Å; only one is shown in Scheme 4b), whereas for **6(HOTf)**, an individual hydrogen bond between the triflate anion (O3) and the N-H group is observed (N1···O3 = 2.804(3) Å).

In order to examine the situation in solution, we have recorded HSQC and HMBC NMR spectra of a mixture of **4** and HOTf in CD_2Cl_2 at –80 °C (see ESI). The data confirm that the nitrogen atom in position 1 is protonated.



Scheme 4. Synthesis of protonated 1-acyl triazenes (a), and molecular structures of **5(HOTf)** (b) and **6(HOTf)** (c) in the solid state. The thermal ellipsoids are at 50% probability. With the exception of NH, hydrogen atoms are not shown for clarity.

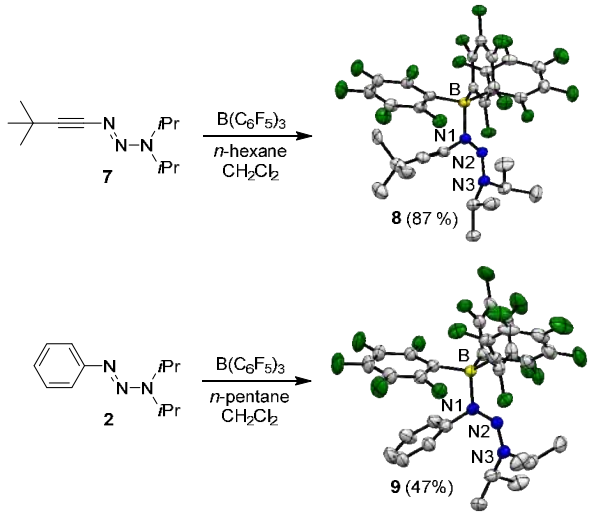
Lewis acid adducts of triazenes

The results summarized in the previous section show that protonation of triazenes preferentially occurs at N1 position. The higher basicity of this site should translate to higher affinity to Lewis acids, given that steric interactions can be neglected.

For our investigations, we have used the strong Lewis acid $B(C_6F_5)_3$. In order to reduce steric interactions between the Lewis acid and the substituent at N1 position, we have first examined reactions with the 1-alkynyl triazene **7** (Scheme 5).[10e,15] A solution of **7** in hexane was added to a solution of $B(C_6F_5)_3$ in dichloromethane/hexane (1:1). The mixture was then stored at –40 °C, resulting in the formation of a yellow precipitate (**8**). Compound **8** was isolated in 87% yield (Scheme 5).

A crystallographic analysis of **8** confirmed that a 1:1 adduct had formed, with the Lewis acid being coordinated to the N1 atom of the triazene. The dative B–N bond has a length of 1.618(3) Å. This value is comparable to what has been reported for adducts of $B(C_6F_5)_3$ with N-donors (see ESI). Interestingly, the bound triazene adopts an unusual *Z* configuration. Most likely, this configuration is favored because it minimizes steric interactions with the bulky Lewis acid. It is worth noting that N1-coordination of the Lewis acid will facilitate an *E* to *Z* isomerization, because the coordination will weaken the N1–N2 bond. For adduct **8**, for example, we observe a rather long N1–N2 bond of 1.303(3) Å.

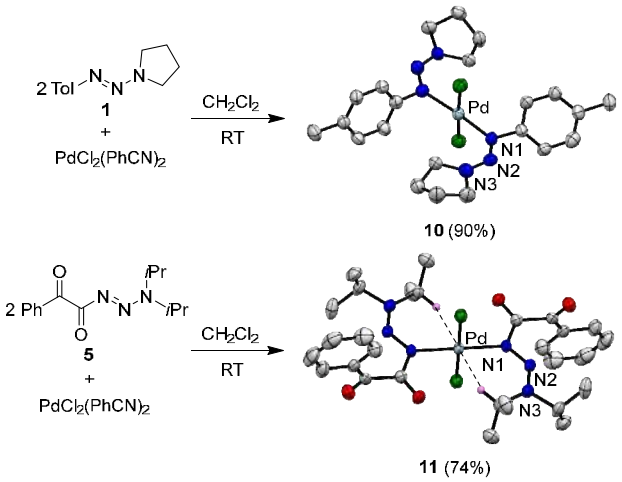
For aryl triazene **2**, we were also able to obtain a $B(C_6F_5)_3$ adduct in crystalline form (**9**). The structure of **9** in the solid state is analogous to that of **8**: the Lewis acid is coordinated to the N1 atom, and the triazene adopts a *Z* configuration (Scheme 5). The bond lengths and angles of **8** and **9** are also similar (Table 1).



Scheme 5. Synthesis of the $B(C_6F_5)_3$ adducts **8** and **9**. The thermal ellipsoids are at 50% probability. Hydrogen atoms are not shown for clarity.

In addition to the boron-based Lewis acid $B(C_6F_5)_3$, we have investigated the interaction of triazenes with $PdCl_2$. This transition metal chloride was chosen because there are several reports about Pd-catalyzed reaction with triazenes,[11b,16] and information about the preferred metal binding site would be valuable for mechanistic considerations. So far, there is very limited information about the coordination of neutral triazenes to transition metals.[10a,17,18]

For our study, we have used aryl triazene **1** and acyl triazene **6**. For solubility reasons, $PdCl_2(PhCN)_2$ was employed instead of plain $PdCl_2$. From mixtures of $PdCl_2(PhCN)_2$ (1 equiv.) and the respective triazene (2 equiv.) in dichloromethane, we were able to obtain the Pd complexes **10** and **11** (Scheme 6). Crystallographic analyses of the complexes revealed that the triazenes act as monodentate ligands with coordination via the N1 atoms. For both complexes, the N1–N2 bonds are longer than the N2–N3 bonds, indicating a strong double bond character of the latter (Table 1). A noteworthy feature of complex **11** is the presence of close C-H···Pd contacts[19] involving two of the four isopropyl groups. In the ^{1}H NMR spectrum of **11**, this interaction is manifested by a strongly deshielded signal for the C*H*Me_2 group at 10.16 pm (CD_2Cl_2).



Scheme 6. The synthesis of the Pd complexes **10** and **11**. The thermal ellipsoids are at 50% probability. Most hydrogen atoms are omitted for clarity.

Conclusions

We have investigated the protonation of 1-aryl, 1-vinyl and 1-acyl triazenes with triflic acid by low temperature NMR spectroscopy and single crystal X-ray analysis. The results show that protonation occurs preferentially at N1 position. This finding is of relevance for the mechanism of the acid-induced cleavage of triazenes, which has been studied extensively over the last years.[4–6] Our data provide experimental evidence that N1-protonated triazenes are more stable than N3-protonated triazenes. The cleavage of 1-aryl-3,3-dialkyl triazenes such as **1** and **2** proceeds via rupture of the N2–N3 bond. Since N1-protonation leads to a strengthening of the N2–N3 bond, it is unlikely that N1-protonated triazenes are productive intermediates during the cleavage reaction. Rather, they should be considered as off-pathway intermediates, which are formed in a reversible fashion upon addition of acid.

Triazenes are also cleaved by strong Lewis acids.[20] We have analyzed adducts of triazenes with $B(C_6F_5)_3$ and $PdCl_2$. The results suggest that N1 is likewise the preferred coordination site of Lewis acids, even though steric interactions might play a role as well. As in the case of Brønsted acids, we assume that N1-bound adducts are off-pathway intermediates in cleavage reactions.

The fact that N1 represents the most basic site is also of relevance for transition metal-catalyzed reactions with triazenes. Given that steric or chelate effects can be neglected, one would assume that neutral triazenes are preferentially coordinated via the N1 atom to the metal center, as observed for the Pd complexes **10** and **11**. This preference should be taken into account for future mechanistic proposals.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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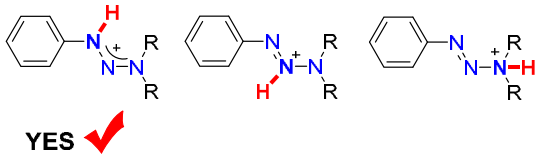
Graphic for the Table of Contents

The relative proton affinity of triazenes



YES