Synthesis and Properties of 1-Acyl Triazenes

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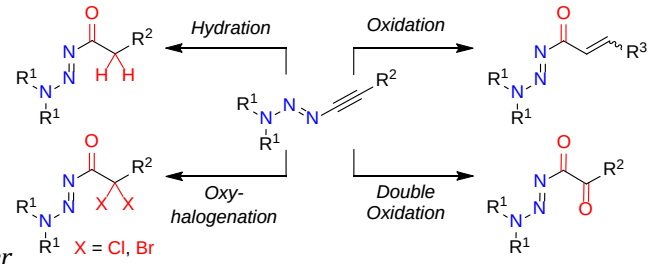


Supporting Information Placeholder

ABSTRACT: 1-Acyl triazenes can be prepared by acid-catalyzed hydration, gold/iodine-catalyzed oxidation, or oxyhalogenation of 1-alkynyl triazenes. Crystallographic analyses reveal a pronounced effect of the acyl group on the electronic structure of the triazene function. 1-Acyl triazenes display high thermal stability, and only moderate sensitivity towards hydrolysis. They are compatible with basic and oxidative conditions, allowing subsequent transformation. Under acidic conditions, 1-acyl triazenes act as acylation reagents.

Triazenes with acyl groups attached to the N3 atom (Figure 1) have been studied extensively over the last decades in medicinal and synthetic chemistry.[1] These compounds are typically prepared by acylation of 1,3-disubstituted triazenes.[1,2] Alternative synthetic pathways include the reaction of deprotonated amides with diazonium salts,[3] the condensation of hydrazides with aromatic nitroso compounds,[4] or the reaction of benzoyl azide with a Grignard reagent.[5] 3-Acyl triazenes have found considerable interest in medicinal chemistry, and numerous bioactive compounds have been reported in the literature.[6] In this context, the reactivity of 3-acyl triazenes has been studied in detail, both from a theoretical[7] and experimental[6,8] point of view. 3-Acyl triazenes have also been used as precursors for aminyl radicals,[9] as acylating agents,[10] and as chemodosimeters for cyanide.[11]

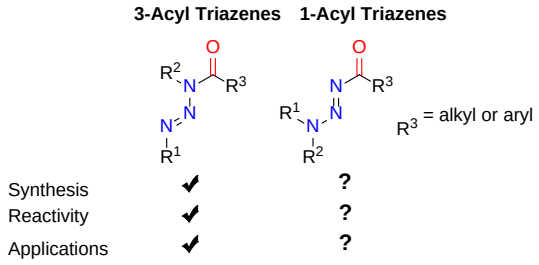


Figure 1. 3-Acyl triazenes versus 1-acyl triazenes.

In contrast to the well-established chemistry of 3-acyl triazenes, there are hardly any reports about triazenes with carbonyl groups attached to the N1 atom. Triazenes with 1-carbamoyl and 1-alkoxycarbonyl groups have been prepared by oxidation of functionalized triazanes.[12] Furthermore, there are reports about benzo[1,2,3]triazine-4(3H)-one derivatives,[13] which can be regarded as cyclic (covalent connection between N1 and N3)[14] acyl triazenes. A general synthetic method for synthesizing acyclic 1-acyl triazenes (Figure 1) is not available so far. We found that 1-acyl triazenes are accessible by hydration or oxidation of 1-alkynyl triazenes, and details about these reactions are given below.

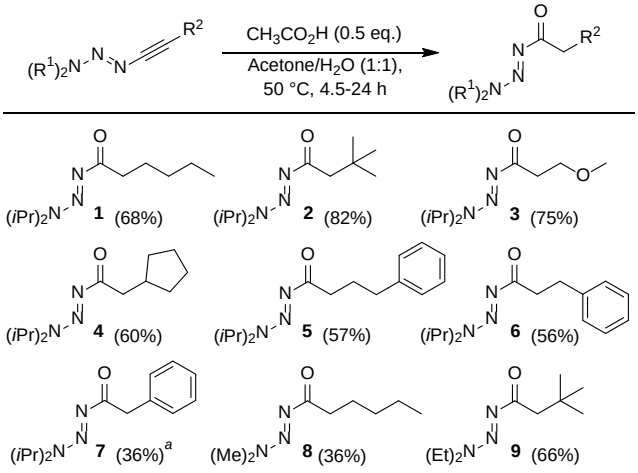
The chemistry described in this report was enabled by our recent discovery that 1-alkynyl triazenes can be prepared from lithium amides, alkynyl Grignard reagents, and nitrous oxide.[15,16] These heteroatom-substituted alkynes display a similar reactivity as ynamides.[17] For example, ketenes react with 1-alkynyl triazenes to give [2+2] cycloaddition products under mild conditions.[17f] Ynamides can be hydrated to give *N*-acyl sulfonamides.[18] An analogous reaction with 1-alkynyl triazenes would give 1-acyl triazenes, and we therefore examined reaction conditions for the controlled hydrolysis of 1-alkynyl triazenes. The published procedures for the hydrolysis of ynamides involve acids or Lewis acids. The triazene group is known to be acid-sensitive.[1] Therefore, the challenge was to find conditions which would allow the hydration of the triple bond without cleavage of the triazene function.

Initial attempts to hydrolyze 1-alkynyl triazenes in the presence of Ag(I) salts showed that the desired products can be formed (see Supporting Information, SI, Table S3.1). However, high catalyst concentrations were needed, and problems with purification were encountered. Switching to

acetic acid catalysis[18b] was found to be advantageous. Moderate to good yields were obtained for alkynyl triazenes containing various substituents at the triple bond (**1**–**6**, Scheme 1). *In-situ* NMR experiments revealed small amounts of $iPr_2NH_2^+$ as side product. The ammonium salt is formed by acid-induced cleavage of the triazene function. However, it is worth noting that the products are less acid-sensitive than a standard aryl triazene (PhN_3iPr_2) under the given conditions (SI, Figure S10.1).

The hydration of a phenylethynyl triazene (R = Ph) turned out to be more difficult. For this substrate, an increased temperature of 100 °C and two equivalents of acetic acid were found to be advantageous. Still, the corresponding acyl triazene **7** was isolated in only 36% yield. Most likely, these hydration reactions are initiated by protonation of the alkyne at the β-carbon atom, and this position is less nucleophilic in the case of the phenylethynyl triazene. Variation of the alkyl substituents at N3 position are possible, as evidenced by the successful synthesis of the acyl triazenes **8** and **9**.

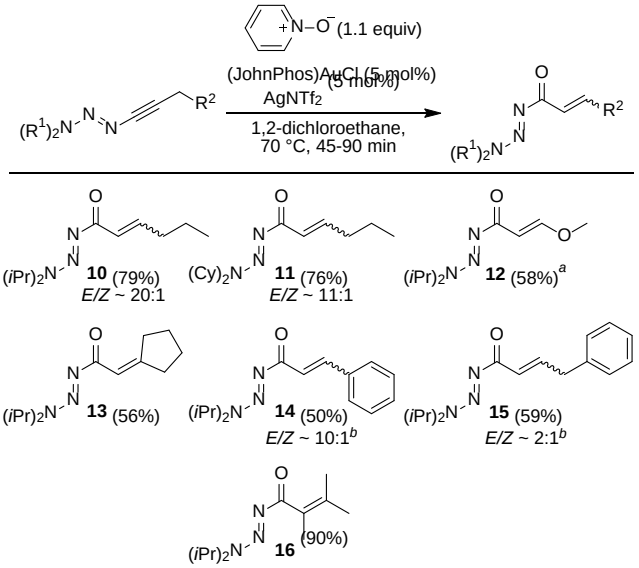
Scheme 1. Acetic Acid-Catalyzed Hydration of Alkynyl Triazenes.



[a] The reaction was performed in a closed vial at 100 °C with 2 equiv CH_3CO_2H.

Next, we have explored the oxidation of 1-alkynyl triazenes with pyridine *N*-oxides in the presence of Au(I) catalysts.[19,20] Screening of different catalysts and reaction conditions showed that (JohnPhos)AuCl in combination with $AgNTf_2$ (both 5 mol %) and pyridine *N*-oxide can be used for the clean formation of the olefinic acyl triazene **10** (SI, Table 4.1). The optimized reactions conditions were then used to synthesize the acryloyl triazenes **11**–**16**, which were obtained in moderate to good yields (Scheme 2). The reactions gave predominantly the *E* isomer. The oxidation of internal alkynes with pyridine *N*-oxides is prone to give mixtures of regioisomers.[21] In our case, oxygen atom transfer was perfectly site-specific, as it was observed for ynamides.[19] The high selectivity can be attributed to the polarization of the triple bond of alkynyl triazenes.[17f] The likely mechanism of the reaction involves a nucleophilic attack of the pyridine *N*-oxide at the Cα position of the Au-activated triple bond, followed by N–O bond rupture and formation of an α-oxo gold carbenoid.[22] Product formation then occurs via a [1,2]H shift (or [1,2]Me shift in the case of **16**).

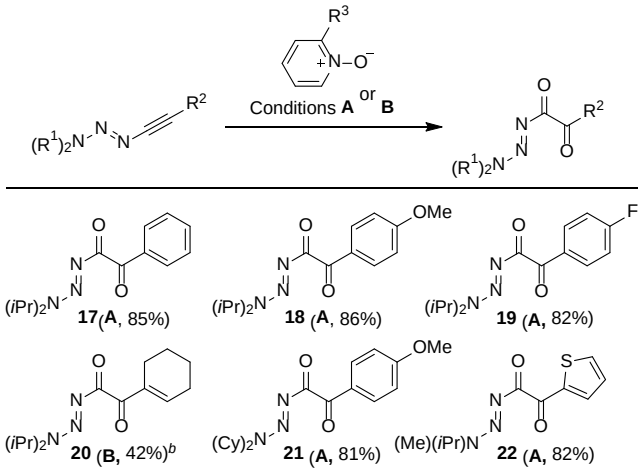
Scheme 2. Au-Catalyzed Oxidation of Alkynyl Triazenes.



[a] Only the *E*-isomer observed. [b] The *E/Z* mixture could not be fully separated.

If [1,2] shifts are not possible, the intermediate gold carbenoid is susceptible to another attack by pyridine *N*-oxide, leading to a double oxidation of the alkyne.[19] Arylethynyl triazenes are not able to undergo [1,2] shifts after a first oxidation, and they appeared to be suited substrates for the synthesis of 1,2-diketones. First test reactions with a phenylethynyl triazene showed that Au-catalyzed double oxidation reactions can indeed be realized when an excess of pyridine *N*-oxide is employed (Scheme 3). However, we also examined if the reaction could be catalyzed by iodine,[23] and the yield for the metal-free oxidation was superior (for **17**: 85 vs. 61%). Triazenes with *p*-methoxyphenyl or *p*-fluorophenyl groups could be oxidized with similar yields (**18** and **19**). When using a triazene with a cyclohexenyl instead of an aryl groups attached to the triple bond, the I_2 activation method was not successful. Here, the Au-catalyzed procedure turned out to be better, allowing the isolation of the diketone **20** in 42% yield. Varying the alkyl substituents on N3 (Cy or Me instead of *i*Pr) gave the corresponding acyl triazenes **21** and **22** in good yields using the I_2-based procedure. It is worth noting that the products are thermally very stable. For compound **17**, for example, we could detect only traces of decomposition after heating a solution in DMSO-d_6 for 5 days at 140 °C.

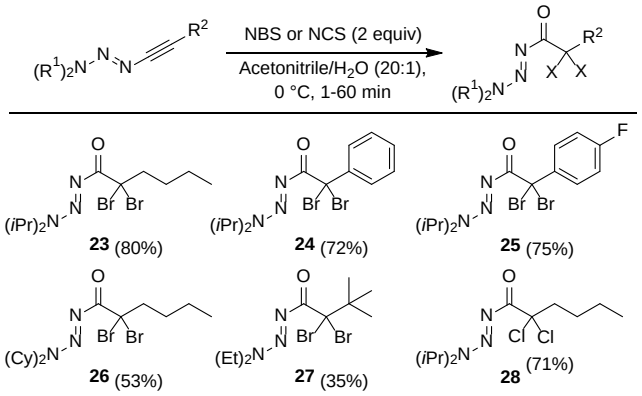
Scheme 3. Double Oxidation of Alkynyl Triazenes.[a]



[a] Conditions **A**: 2-chloro pyridine *N*-oxide (R^3 = Cl, 3 equiv), I_2 (0.5 equiv), acetonitrile (0.1 M), rt, 50 min, conditions **B**: pyridine *N*-oxide (R^3 = H, 2.2 equiv), (JohnPhos)AuCl (10 mol %), $AgNTf_2$ (10 mol %), 1,2-dichloroethane (0.2 M), 70 °C, 1.5 h. [b] Only conditions **B** gave the desired product.

To expand the scope even further, we examined oxyhalogenation reactions[24] with alkynyl triazenes. Using *N*-bromosuccinimide (NBS), we were able to obtain the dibrominated 1-acyl triazenes **23**–**27** in mostly good yields (Scheme 4). The reactions can be performed under mild conditions (0 °C) without a catalyst, which is in contrast to most oxyhalogenation reactions with NBS described in the literature.[24,25] We attribute the ease of the transformation to the high intrinsic reactivity of the alkynyl triazenes. Changing NBS to *N*-chlorosuccinimide (NCS) led to the formation of α-dichlorinated acyl triazene **28** in 71% yield. With *N*-iodosuccinimide (NIS), on the other hand, we were not able to prepare the corresponding diiodo compound.

Scheme 4. Oxyhalogenation of 1-Acyl Triazenes.



After having established methodologies for the synthesis of four types of 1-acyl triazenes, we focused on exploring the properties of these new compounds. The solid state structures of **2**, **11-*E***, **16**, **18**, **20** and **21** were determined by single crystal X-ray diffraction (Figure 2a).

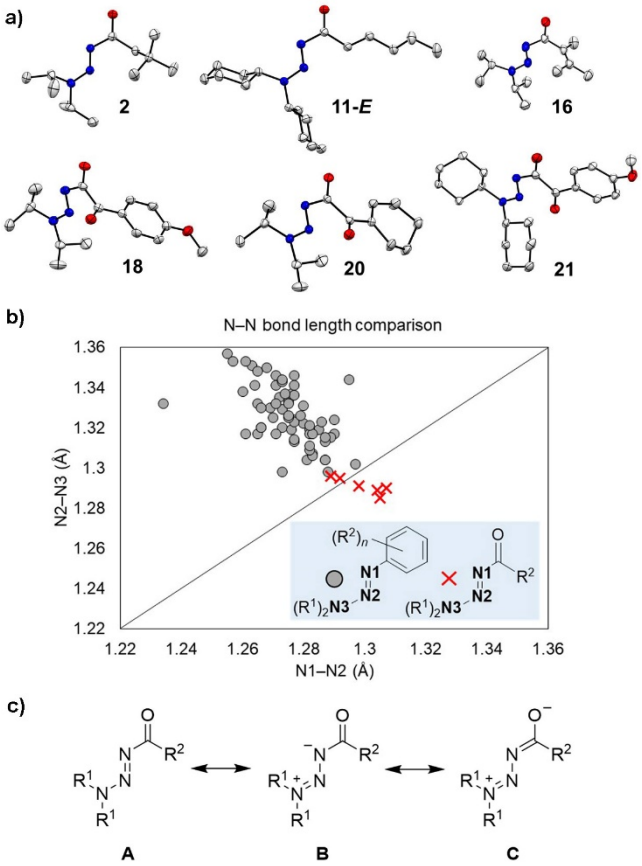


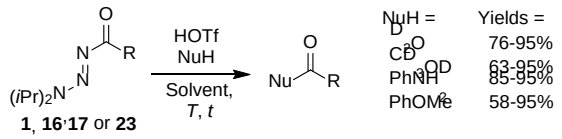
Figure 2. Crystal structures of 1-acyl triazenes (a), N–N bond lengths of 1-aryl- and 1-acyl triazenes (b), and mesomeric structures of 1-acyl triazenes (c).

For all six compounds, the N–C=O group was found to be in plane with the triazene group, indicating electronic communication between the two. The electron-withdrawing effect of the carbonyl group has a strong effect on the structure of the triazene. Notably, the formal N–N single bond between N3 and N2 is of comparable length as the formal N=N double bond between N2 and N1 (for **16**, **18**, **20**, and **21**, the N2–N3 bond is even shorter than the N1–N2 bond). The pronounced influence of the acyl group is evident when comparing the structures of 1-acyl triazenes with what is found for 3,3-dialkyl-1-aryl triazenes. An analysis of 67 compounds found in the CCDC database showed that these triazenes all display a 'normal' behavior, with the formal N–N single bond being longer than the formal N=N double bond ($N2–N3_{av.}$ = 1.33 Å, $N1–N2_{av.}$ = 1.27 Å; Figure 2b). The remarkably short N2–N3 bonds of 1-acyl triazenes imply that the resonance forms **B** and **C** contribute significantly to describing the electronic structure (Figure 2c).[26]

3-Acyl triazenes are known to undergo facile hydrolysis.[8c] In order to assess the hydrolytic stability of 1-acyl triazenes, we have analyzed solutions of **3** in D_2O/d_6-acetone (4:1) by NMR spectroscopy (compound **3** was chosen because its solubility in aqueous solution). After heating for 12 days at 50 °C, only partial hydrolysis was observed (28%). Heating for 22 hours to reflux resulted in 61% hydrolysis. These results show that 1-acyl triazenes have a comparatively low susceptibility to hydrolyze.

As mentioned earlier, triazenes are acid sensitive compounds. Protonation typically induces cleavage of the N2–N3 bond, with concomitant formation of ammonium and diazonium ions.[1] In the case of 1-acyl triazenes, acid-induced N2–N3 bond cleavage would give highly reactive acyldiazonium compounds, which would act as acylation agents. In order to examine if such reactivity can indeed be observed, we have analyzed reactions of the 1-acyl triazenes **1**, **16**, and **17** with HOTf in the presence of different nucleophiles (water, methanol, aniline, and anisole). In most cases, a clean acylation reaction was observed (Scheme 5, for details, see SI). Attempts to perform more challenging acylation reactions with benzene as nucleophile were not successful. We have also examined acylation reactions with the brominated triazene **23**. With water and methanol, the expected products were obtained in 76 and 94% yield, respectively, but reactions with anisole and aniline gave a mixture of products, and more detailed analyses were not performed.

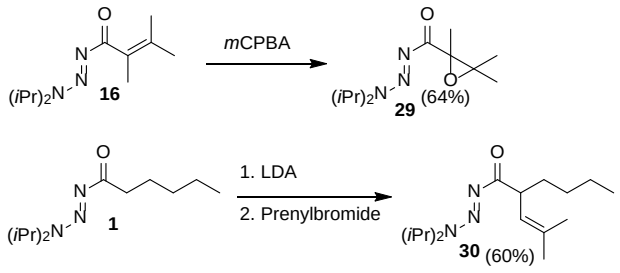
Scheme 5. 1-Acyl Triazenes as Acylating Agents.[a]



[a] Yields and product ratios were determined by ^{1}H NMR spectroscopy. Conditions: HOTf (2 equiv), NuH = D_2O: CD_3CN/D_2O, 9:1, 0.05 M, rt (for **23**: 70 °C), 11 – 90 min; NuH = CD_3OD: neat, 0.05 M, rt, 44 – 59 min; NuH = aniline (2 equiv): CD_3CN (0.05 M), 70 °C, 70 min – 18 h; NuH = anisole (2 equiv): CD_3CN (0.05 M), 70 °C, 20 – 21 h.

Finally, we have briefly examined reactions under non-acidic conditions (Scheme 6). Oxidative conditions are compatible with the triazene function, as evidenced by the synthesis of epoxide **29**. Strongly basic conditions are also tolerated, and we were able to perform an alkylation reaction with prenylbromide via an enolate intermediate generated by LDA (**30**).

Scheme 6. Reactions of the 1-acyl triazenes 16 and 1.[a]



[a] Conditions: **29**: DCM (0.2 M), *m*CPBA (1.1 equiv), rt, 2 h, isolated yield; **30**: LDA (1.42 equiv), prenylbromide (1.5 equiv) in THF, –78 °C, isolated yield.

To conclude: we have shown that 1-acyl triazenes can be prepared by hydrolysis or oxidation of 1-alkynyl triazenes. Using these methods, we were able to synthesize for the first time a variety of structurally diverse 1-acyl triazenes. The acyl group at N1 position was found to have a strong influence on the physical and chemical properties of the triazenes. Crystallographic analyses revealed extremely short N2–N3 bond lengths. Accordingly, the energy barrier for rotation around this bond is much higher than what has been reported for other triazenes. The new 1-acyl triazenes are thermally robust compounds with a low susceptibility to hydrolyze. Under acidic conditions, they act as acylating agents. Basic or oxidative conditions, on the other hand, are well tolerated by the triazene function.

In the present work, we have focused on the synthesis and the properties of 1-acyl triazenes. However, investigating the biological activity of these compounds appears worthwhile. The bioactivity of previously reported triazenes is generally related to the fact that they represent masked alkylating agents.[1,6] 1-Acyl triazenes act as masked acylating- rather than alkylating agents. Therefore, these compounds might display a biological activity which is distinct from that of other triazenes.

ASSOCIATED CONTENT

Supporting Information

Experimental details and analytical data of the new compounds (PDF). Crystallographic data for compounds **2**, **11-*E***, **16**, **18**, **20** and **21** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This work was supported by funding from the Swiss National Science Foundation and from the Ecole Polytechnique Fédérale de Lausanne (EPFL).

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(25) For the oxyhalogenation of alkynes with NXS reagents, ionic and radical mechanisms have been discussed. In our case, the involvement of radicals seems likely because the reaction was found to be light sensitive. When the synthesis of **23** was performed in the strict absence of light, we were able to detect a significant amount of a mono-brominated acyl triazene in addition of **23**. When the reactions was carried out under ambient light, the mono-brominated triazene was not detected.

(26) A high energy barrier for rotation around the N2–N3 bond was confirmed by VT-NMR experiments. For details, see the SI.