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Conversion of simple alkenes into 1*H*-1,2,3-triazolium salts by oxidative cycloaddition and subsequent dehydrogenation†

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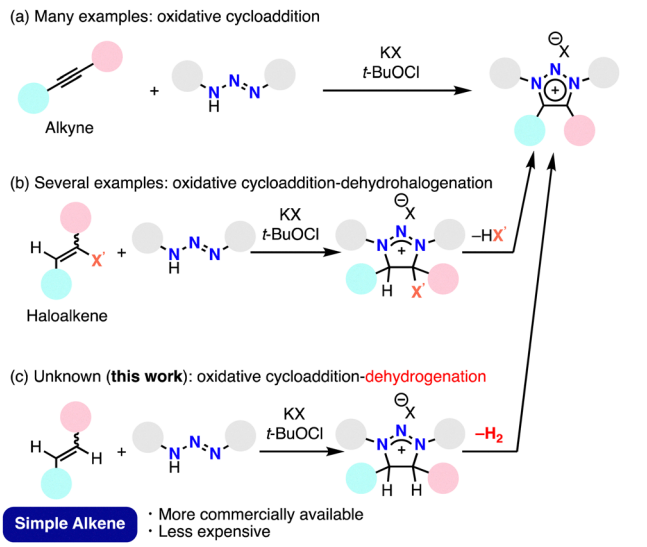
A new method for the synthesis of 1*H*-1,2,3-triazolium salts from triazenes and simple alkenes has been developed. The oxidative [3+2] cycloaddition of triazenes with alkenes affords 4,5-dihydro-1*H*-1,2,3-triazolium salts, which undergo dehydrogenative aromatization under remarkably mild conditions (using potassium bicarbonate in air at room temperature) to provide 1*H*-1,2,3-triazolium salts. This method exhibits broad functional group tolerance and enables the synthesis of a triazolium-based diol, which serves as a cationic diol monomer for cationic polymer synthesis.

1*H*-1,2,3-Triazolium salts have been used as cationic scaffolds across various fields, including materials science,[1] supramolecular chemistry,[2] and organocatalysis.[3] Moreover, deprotonation of 1*H*-1,2,3-triazolium salts provides 1,2,3-triazol-5-ylidenes,[4] which possess superior electron-donating properties compared to conventional N-heterocyclic carbenes such as imidazol-2-ylidenes. Consequently, extensive efforts have been directed towards developing methods for the synthesis of 1*H*-1,2,3-triazolium salts. The most common approach involves the *N*-alkylation of preformed 1*H*-1,2,3-triazoles, which are readily synthesized *via* the copper-catalyzed [3+2] cycloaddition of azides and alkynes (click reaction).[5] The remarkable efficiency and high functional-group tolerance of the click reaction have enabled the synthesis of structurally diverse 1*H*-1,2,3-triazolium salts. Heterocyclic frameworks of triazolium salts have also been constructed through the oxidative [3+2] cycloaddition of triazenes and alkynes (Scheme 1a).[6] Notably, this one-step method provides more direct access to triazolium salts than the previously described cycloaddition-alkylation sequence, can be performed in air, and exhibits highly functional group tolerance. Moreover, haloalkenes can be used as reaction partners instead of alkynes in triazolium salt syntheses.[6b,7] In this case, oxidative cycloaddition initially yields 4,5-dihydro-1*H*-1,2,3-triazolium salts, which undergo dehydrohalogenation to afford 1*H*-1,2,3-triazolium salts (Scheme 1b). Since a halogen substituent is required for the aromatization step, simple alkenes cannot be used in the synthesis of 1*H*-1,2,3-triazolium salts. Given that the number of commercially available simple alkenes is significantly higher than that of alkynes, developing a synthetic method for triazolium salts using alkenes would be expected to greatly expand their structural diversity. Herein, we report that the cycloaddition of triazenes with alkenes, followed by base-promoted dehydrogenative aromatization, affords 1*H*-1,2,3-triazolium salts (Scheme 1c).



Scheme 1 Oxidative cycloaddition of triazenes and unsaturated hydrocarbons.

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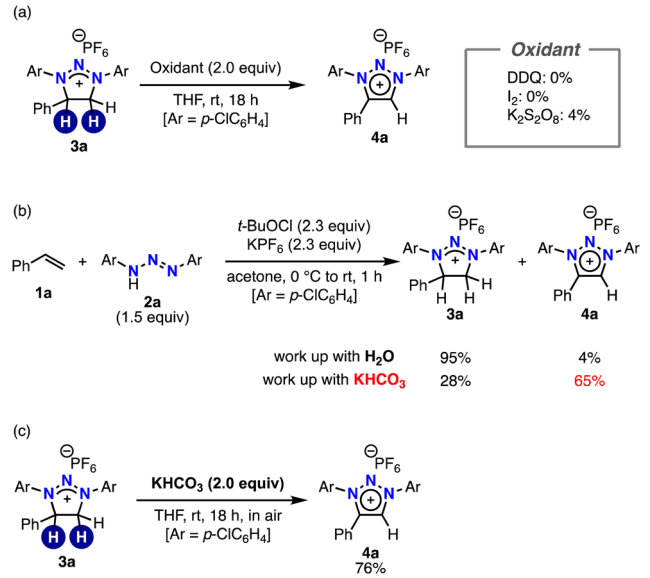
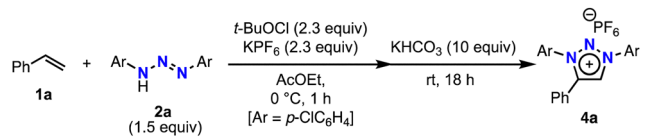


Scheme 2 (a) Examination of oxidants. (b) Unexpected formation of triazolium salt **4a**. (c) Base-promoted dehydrogenation of dihydrotriazolium salt **3a**.

Dehydrogenative aromatization of neutral heterocycles in the presence of an oxidant is widely reported,[8] but no studies have explored its application to cationic heterocycles. We first examined various oxidants for the dehydrogenation of dihydro-1*H*-1,2,3-triazolium salt **3a**, which was prepared by the oxidative [3+2] cycloaddition of triazene **1a** and alkene **2a**. Treatment of **3a** with DDQ, a common oxidant for dehydrogenative aromatization of neutral heterocycles, at room temperature for 18 h resulted in no formation of the desired product **4a** (Scheme 2a). The reaction did not proceed even at 90 °C. Other oxidants, including molecular iodine and potassium peroxodisulfate, were also ineffective in this reaction. The low reactivity of **3a** toward oxidants may be attributed to its electron-deficient nature. However, we unexpectedly obtained **4a** in 4% yield when the reaction of **1a** and triazene **2a** was quenched with water (Scheme 2b). Surprisingly, using potassium bicarbonate instead of water in the quenching process increased the product yield up to 65%. Encouraged by this result, we performed the reaction of **3a** with potassium bicarbonate at 30 °C in air, affording **4a** in high yield (Scheme 2c). While several examples of base-promoted aerobic heterocycle dehydrogenation have been reported, they typically require harsh conditions, such as the use of *t*-BuOK at 140 °C.[9] In contrast, our reaction conditions—potassium bicarbonate at 30 °C—are exceptionally mild for aerobic heterocycle dehydrogenation.

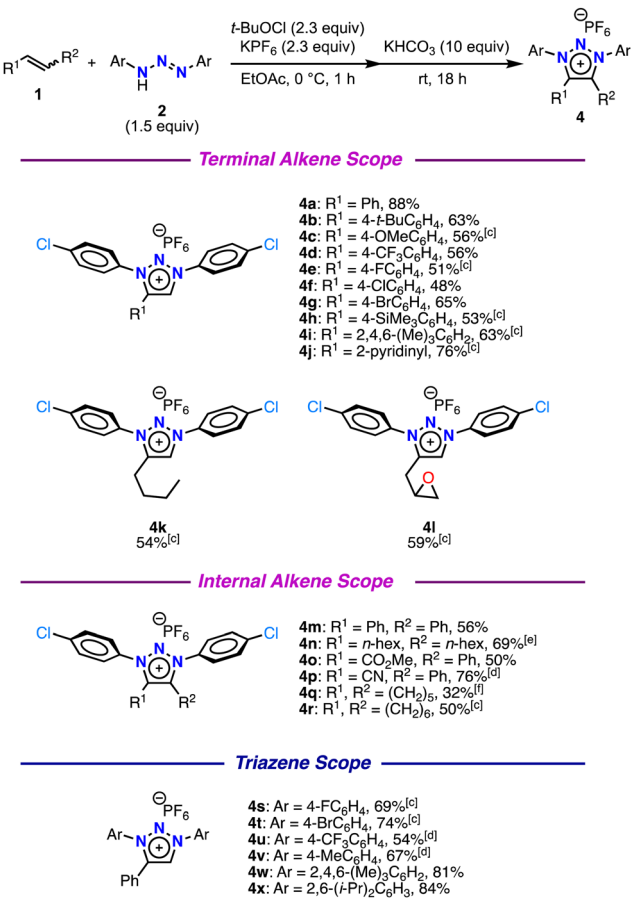
Next, we investigated the effects of solvents and bases on the oxidative cycloaddition of **1a** and **2a**, followed by the subsequent dehydrogenative aromatization (Table 1). The reaction of **1a** and **2a** in the presence of *t*-butyl hypochlorite and potassium

Table 1 Effect of solvents and bases[a]



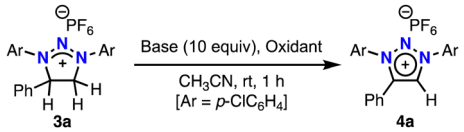
Entry	Variation from the standard conditions	Yield[b] (%)
1	None	94
2	Acetone, instead of AcOEt	77
3	CH_3CN, instead of AcOEt	83
4	THF, instead of AcOEt	61
5	CH_2Cl_2, instead of AcOEt	58
6	$NaHCO_3$, instead of $KHCO_3$	35
7	K_2CO_3, instead of $KHCO_3$	87
8	KOH, instead of $KHCO_3$	81
9	Pyridine, instead of $KHCO_3$	9
10	Et_3N, instead of $KHCO_3$	81
11	DBU, instead of $KHCO_3$	42

[a] Standard conditions: **1a** (0.20 mmol), **2a** (1.5 equiv.), *t*-BuOCl (2.3 equiv.), KPF_6 (2.3 equiv.) in AcOEt (1.0 mL) at 0 °C for 1 h; $KHCO_3$ (10 equiv.) at room temperature for 18 h. [b] Determined by ^1H NMR analysis of the crude reaction mixture using dibromomethane as the internal standard.



Scheme 3 Reaction scope. [a] Standard reaction conditions: **1** (0.50 mmol), **2** (1.5 equiv.), *t*-BuOCl (2.3 equiv.), KPF_6 (2.3 equiv.) in AcOEt at 0 °C to rt for 1 h; $KHCO_3$ (10 equiv.) at room temperature for 18 h. [b] Isolated yields. [c] **1** (0.50 mmol), **2** (1.2 equiv.), *t*-BuOCl (2.3 equiv.), KPF_6 (2.3 equiv.) in AcOEt at 0 °C to rt for 1 h; K_2CO_3 (10 equiv.) at room temperature for 1 h. [d] **1** (0.50 mmol), **2** (1.2 equiv.), *t*-BuOCl (2.3 equiv.), KPF_6 (2.3 equiv.) in AcOEt at −30 °C for 5 h.; K_2CO_3 (10 equiv.) at −30 °C for 24 h. [e] **1** (0.50 mmol), **2** (1.5 equiv.), *t*-BuOCl (2.3 equiv.), KPF_6 (2.3 equiv.) in AcOEt at 0 °C to rt for 1 h; K_2CO_3 (10 equiv.) at room temperature for 1 h.

Table 2 Effect of base and oxidant on the dehydrogenative aromatization[a]



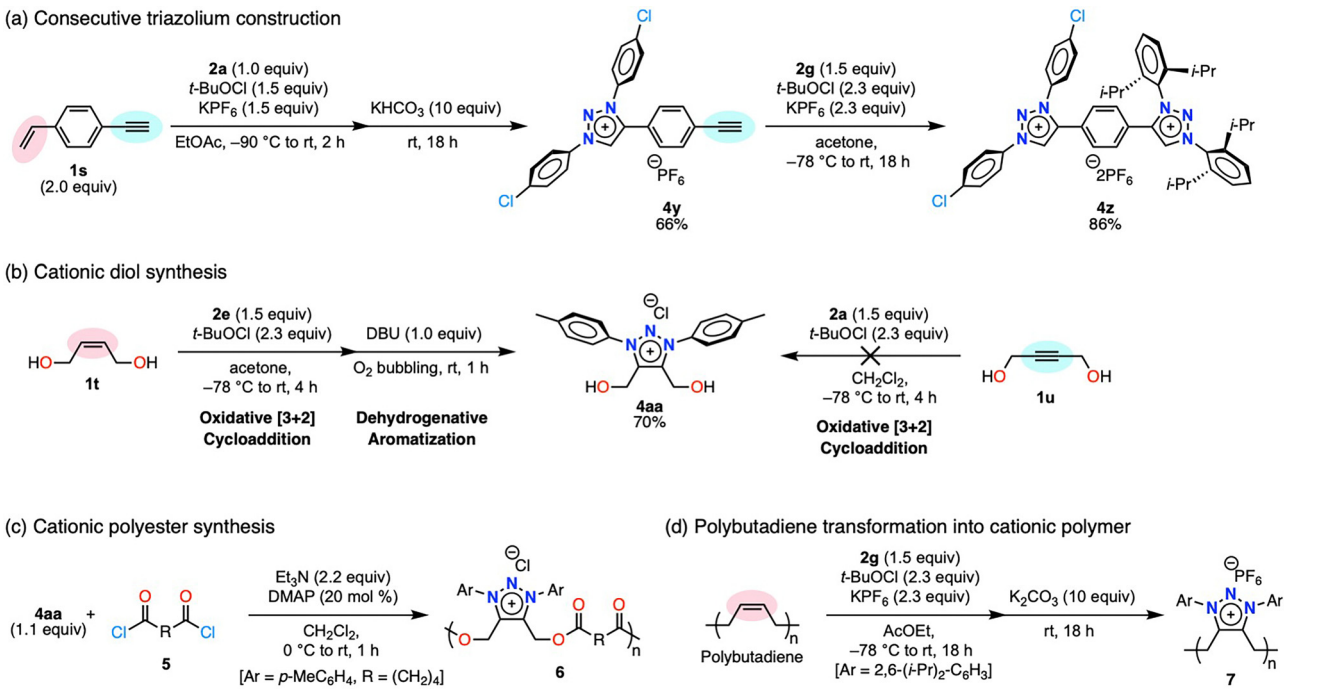
Entry	Oxidant	Base	Conversion[b] (%)	Yield[b] (%)
1	—	$KHCO_3$	9	6
2	Air	$KHCO_3$	50	42
3	O_2 balloon	$KHCO_3$	100	98
4	O_2 balloon	—	3	0
5	$K_2S_2O_8$	$KHCO_3$	11	7
6[c]	I_2	$KHCO_3$	3	0

[a] Standard conditions: **3a** (0.50 mmol), base (10.0 equiv.) in CH_3CN (2.5 mL) at room temperature for 1 h. [b] Determined by ^1H NMR analysis of the crude reaction mixture using dibromomethane as the internal standard. [c] Oxidant (2.0 equiv.)

hexafluorophosphate in ethyl acetate at 0 °C for 1 h, followed by the addition of potassium bicarbonate and stirring at room temperature for 18 h, afforded triazolium salt **4a** in 94% yield. While other solvents, such as acetone, acetonitrile, tetrahydrofuran, and dichloromethane, also promoted the reaction (entries 2–5), ethyl acetate proved to be the most effective (entry 1). When the dehydrogenative aromatization was performed using sodium bicarbonate, the product yield decreased to 35% (entry 6). Potassium carbonate and potassium hydroxide also gave **4a** in high yields, though small amounts of unidentified byproducts were observed. Among the organic bases screened, triethylamine proved to be the most efficient for the dehydrogenative aromatization (entries 9–11).

With the optimized reaction conditions in hand, the scope of alkenes in the triazolium salt synthesis was examined (Scheme 3). Notably, all triazolium products **4** were purified only by washing with diethyl ether. Aryl-substituted alkenes with electron-donating and electron-withdrawing groups were successfully converted into the corresponding 1*H*-1,2,3-triazolium salts **4a–d** in moderate to good yields. Halogen and silyl groups were well tolerated in the reaction (**4e–h**), and neither steric hindrance (**4i**) nor Lewis-basic functionality (**4j**) hindered the reaction. Alkyl-substituted alkenes provided the corresponding products **4k** and **4l**, while various internal disubstituted alkenes also participated successfully (**4m–p**). Moreover, cyclic alkenes, such as cyclopentene and cyclohexene, produced triazolium-fused carbocycles **4q** and **4r**. We next investigated the scope of triazenes in the reaction. Triazenes bearing both electron-withdrawing and electron-donating substituents on aromatic rings yielded the corresponding products **4s–v** in good yields. Sterically hindered aromatic substituents did not negatively affect the reaction (**4w** and **4x**).

To gain mechanistic insights into the dehydrogenative aromatization of dihydrotriazolium salts, we performed several control experiments (Table 2). Under a nitrogen atmosphere and in the presence of potassium bicarbonate, **4a** was obtained in only 6% yield (entry 1). In contrast, the yield increased to 42% when the reaction was performed in air (entry 2), and an oxygen atmosphere allowed the reaction to proceed quantitatively (entry 3). Notably, no product formation was observed without a base (entry 4). Moreover, other oxidants commonly used for the dehydrogenative aromatization of neutral heterocycles were ineffective in this reaction (entries 5 and 6). These results highlight the essential role of both molecular oxygen



Scheme 4 Synthetic applications.

and base in dehydrogenative aromatization. The plausible reaction mechanism is shown in Scheme S1 (ESI†).

To demonstrate the practicality of the method, we performed the reaction of **1a** and **2a** on a 20 mmol scale, affording product **4a** in 49% yield (5.4 g) (Scheme S2, ESI†). We then explored the synthesis of bistriazolium salt **4z**, which contains two different substituents on the triazolium nitrogen atoms (Scheme 4a). This approach was motivated by DFT calculations, which revealed that the activation barrier for the oxidative [3+2] cycloaddition of triazenes and alkenes is lower than that for alkynes (Fig. S1, ESI†). Indeed, when aryl-substituted alkene **1s**, featuring an alkynyl functionality, was reacted with triazene **2a** at −90 °C, followed by a dehydrogenative process, the alkynyl-functionalized triazolium salt **4y** was obtained in good yield. Subsequent treatment of **4y** with diisopropylphenyl-substituted triazene **2g** afforded **4z** in high yield. This compound might be used to prepare heterobimetallic NHC complexes *via* sequential deprotonative metalation because of the difference in steric environments between these deprotonative protons. Furthermore, this method enabled the synthesis of triazolium-based diol **4aa**, which is challenging to prepare using alkynes as starting materials due to the lower reactivity of alkyne **1u** compared to alkene **1t** (Scheme 4b). As a preliminary result, this diol **4aa** was successfully applied for the polycondensation with diacyl chloride **5**, affording triazolium-based cationic polyester **6** (Scheme 4c). In addition, the oxidative cycloaddition–dehydrogenation strategy enabled the transformation of polybutadiene into triazolium-based polymer **7** (Scheme 4d). As cationic polymers have been widely used in various fields, including medicinal chemistry[10] and materials science,[11] the properties and applications of these cationic polymers will be investigated in the future work.

In conclusion, we developed a method for the preparation of 1*H*-1,2,3,-triazolium salts *via* the oxidative [3+2] cycloaddition of triazenes and alkenes, followed by dehydrogenation. Notably, the dehydrogenative aromatization proceeded under milder reaction conditions compared to those for neutral heterocycles probably due to the distinct electronic properties of dihydrotriazolium salts. This method has a broad substrate scope and could be applied to cationic polymer synthesis.

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Data availability

The data underlying this study are available in the published article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

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