

Skeletal Transformation of Unactivated Arenes Enabled by a Low-Temperature Dearomative (3+2) Cycloaddition

Sajan Pradhan, Fahimeh Mohammadi, and Jean Bouffard*

Department of Chemistry and Nanoscience, Ewha Womans University, Seoul 03760, Korea

*bouffard@ewha.ac.kr

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ABSTRACT: Simple aromatic compounds like benzene are abundant feedstocks, for which the preparation of derivatives chiefly begins with electrophilic substitution reactions, or less frequently reductions. Their high stability makes them particularly reluctant to participate in cycloadditions under ordinary reaction conditions. Here we demonstrate the exceptional ability of 1,3-diaza-2-azoniaallene cations to undergo formal (3+2) cycloadditions with unactivated benzene derivatives, below room temperature, to provide thermally stable dearomatized adducts on a multi-gram scale. The cycloaddition, which tolerates polar functional groups, activates the ring toward further elaboration. On treatment with dienophiles the cycloadducts undergo a (4+2) cycloaddition-cycloreversion cascade to yield substituted or fused arenes, including naphthalene derivatives. The overall sequence results in the transmutation of arenes through an exchange of the ring's carbons: a two-carbon fragment from the original aromatic ring is replaced with another from the incoming dienophile, introducing an unconventional disconnection for the synthesis of ubiquitous aromatic building blocks. Applications of this two-step sequence to the preparation of substituted arenes, isotopically labeled molecules, and medicinally relevant compounds are demonstrated.

INTRODUCTION

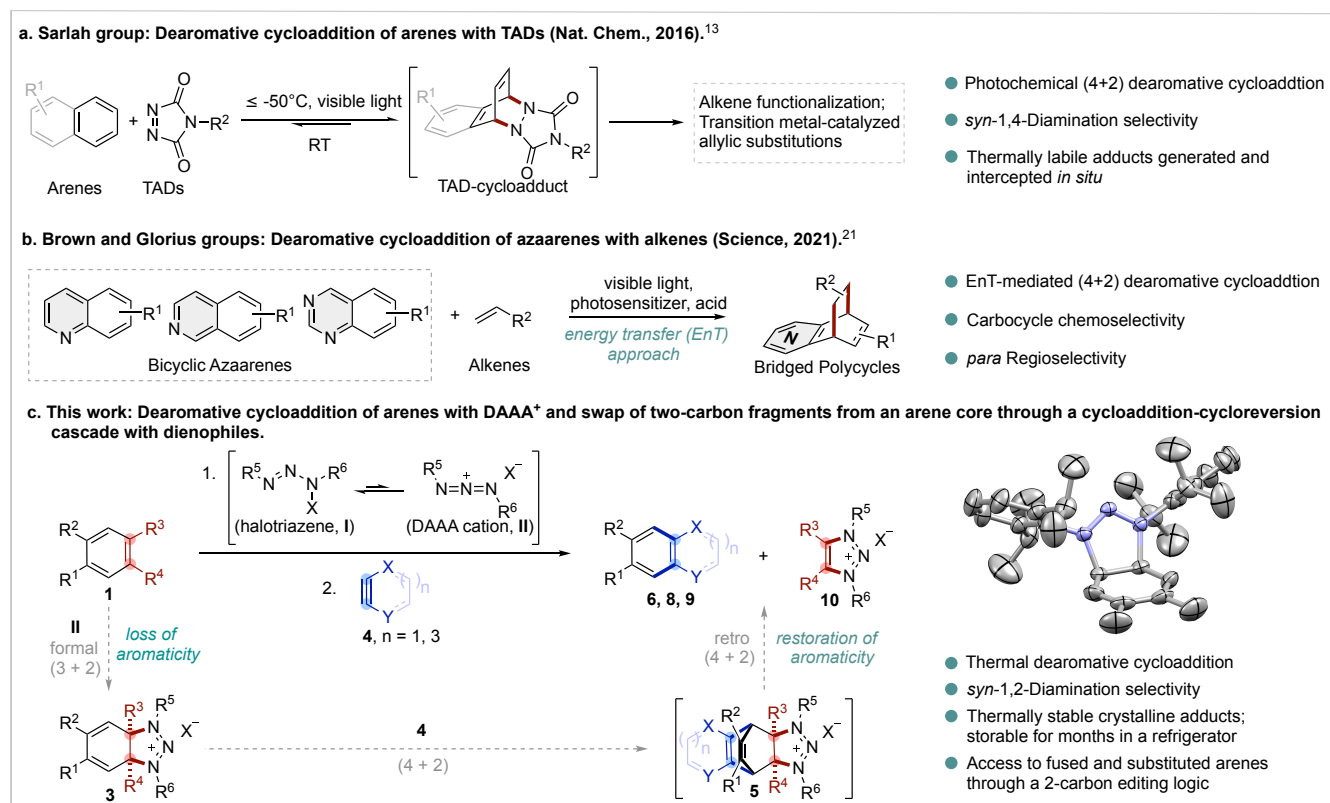
Substitution reactions prevail in the chemistry of arenes, owing to the stability gains that drive rearomatization following the addition of electrophiles, nucleophiles or radicals. Substitutions also predominate celebrated advances in synthetic transformations of arenes, from cross-couplings to late-stage C–H functionalization.¹ A number of aromatic dienes, such as furan, and fused (hetero)arenes with modest resonance energies readily participate in dearomative cycloadditions.² However, intermolecular cycloadditions³ of benzene rings that are neither strained⁴ nor electronically⁵ activated seldom occur under pressures and temperatures that are conducive to their application in organic synthesis.⁶ Notable exceptions include cycloadditions carried out photochemically,⁷ through prior coordination of the arene to a transition metal complex,⁸ or else with exceptionally reactive reaction partners such as activated arynes,⁹ and carbenes or metal carbenoids.^{10,11}

Among recent advances in intermolecular dearomative cycloadditions of unactivated arenes, two series of reports are notable in the context of the work presented herein. Beginning in 2016, the Sarlah group reported that the (4+2) photoadducts of simple arenes and 1,2,4-triazoline-3,5-diones (TADs),¹² though thermally unstable above -10°C in the case of monocyclic arenes, could be successfully intercepted at low temperatures with suitable reagents (Scheme 1a). Through dihydroxylations,¹³ reductions,¹⁴ catalytic allylic substitutions,¹⁵ hydroborations,¹⁶ epoxidations,¹⁷ and cyclopropanations,¹⁸ among others,¹⁹ the initial cycloadducts were elaborated to provide polysubstituted carbocycles.²⁰ In 2021, the Brown and Glorius groups jointly reported that triplet photosensitization enabled the *para*-cycloaddition of

alkenes with quinolines, isoquinolines or quinazolines under acidic conditions (Scheme 1b).²¹ Triplet photosensitization was also successfully extended to the intermolecular (4+2) photocycloaddition of alkenes with electron-poor naphthalenes.²² Related photosensitized (4+2) cycloadditions between alkenes and pyridine or benzene derivatives have also been reported, albeit only intramolecularly.^{3a,23,24}

During studies on mesoionic carbenes prepared by the (3+2) cycloaddition between alkynes and 1,3-diazazoniaallene cations (DAAA⁺, **II**),^{25,26} we observed the unexpected interception of aromatic cosolvents by **II**, resulting in the formation of dearomatized cycloadducts whose structure was confirmed by an X-ray diffraction experiment (**3a**, Scheme 1c). Whereas the reactive 1,3-dipoles **II** have earlier been shown to participate in cycloaddition reactions with alkenes, alkynes, carbodiimides, cyanamides and C₆₀,^{27,28} their cycloadditions with arenes are not precedented. Here we report the optimization of this unexpected dearomative cycloaddition and its scope. Moreover, we illustrate its synthetic utility, using a cycloaddition-cycloreversion sequence, to transform simple aromatic rings into substituted or fused arene derivatives through the excision of a two-carbon fragment from their core and the subsequent transplantation of a subrogate fragment therein (Scheme 1c). To accomplish this goal, arenes (**1**) first undergo a dearomative cycloaddition with DAAA⁺ **II** to furnish the formal (3+2) adducts **3**. Then, the cyclohexadiene-containing adducts **3**, undergo a (4+2) cycloaddition with dienophiles **4** to generate the transient intermediate **5**, which cycloreverts to provide the modified arenes (**6**, **8** and **9**) as the desired products and the triazolium cation **10** as byproduct.

Scheme 1. (a-b) Recently reported dearomative (4+2) cycloadditions of arenes and azaarenes; (c) Dearomative cycloaddition of arenes with DAAA⁺ and its application for the synthesis of substituted and fused arenes through a cycloaddition-cycloreversion cascade; Inset: X-ray structure of adduct **3a (50% thermal ellipsoids) in the solid state; hydrogens and PF₆⁻ counter-ion were removed for clarity.**



RESULTS AND DISCUSSION

Development of a dearomative cycloaddition reaction of arenes. Investigations of the dearomative cycloaddition were first carried out using *o*-xylene **1a**, 1,3-bis(2,6-diisopropylphenyl)triazene (**2a**), *t*-BuOCl and KPF₆ in CH₂Cl₂ from -78 °C to room temperature (Table 1). Under these conditions previously reported for the preparation of 1,3-diazolium salts,^{25b} the fused triazolium cycloadduct **3a** was obtained in 57% yield (entry 1). After filtration of insoluble inorganic salts and evaporation of the volatiles, the product **3a** was purified by simple trituration in diethyl ether; chromatographic separation was unnecessary. The structure of **3a** was unambiguously confirmed by NMR and a single-crystal X-ray diffraction experiment (Scheme 1c). The influence of the different reaction parameters was next assessed (Table 1; for full optimization details, see also Table S1). The reaction was compatible with several moderately polar organic solvents, among which THF gave the best results (76%, entry 3). No precautions to exclude moisture or oxygen were necessary, and solvents taken directly from a previously opened bottle exposed to moist air did not depress the reaction yields. Oxidation of the 1,3-diazolium salt **2a** to the halogenated precursor **I** was best accomplished with *t*-BuOCl; other oxidants did not perform as well as the hypochlorite. Among Lewis acids added to promote the ionization of the putative *N*-halotriazene intermediate **I** to the reactive DAAA⁺ **II**, the mild KPF₆ improved yield and purity, and gave crystalline adducts (e.g., **3a**·PF₆) as well (entries 3-5).

Table 1. Optimization of the dearomative (3+2) cycloaddition between arenes and DAAA⁺ cations.

Entry	Lewis acid	Solvent	Additive, Temperature	Yield ^d 3a
1	KPF ₆	CH ₂ Cl ₂	-78 °C–RT	57%
2	KPF ₆	EtOAc	-78 °C–RT	66%
3	KPF ₆	THF	-78 °C–RT	76%
4	NaOTf	THF	-78 °C–RT	47%
5	SbCl ₅	THF	-78 °C–RT	61%
6	KPF ₆	THF	HFIP, -78 °C–RT	81%
7	KPF ₆	THF	HFIP, -40 °C–RT	73%
8	KPF ₆	THF	HFIP, -20 °C–RT	58%
9 ^b	KPF ₆	THF	HFIP, 0 °C–RT	nr
10 ^c	KPF ₆	THF	HFIP, -78 °C–RT	66%

^aReaction conditions: **1a** (1 mL), **2a** (1 mmol), *t*-BuOCl (1 mmol), Lewis acid (1.1 mmol), additive (1 mmol), and solvent (4.5 mL). ^bnr denotes no reaction. ^cLarger-scale synthesis of **3a** performed using **2a** on a 5-mmol scale. ^dIsolated yields.

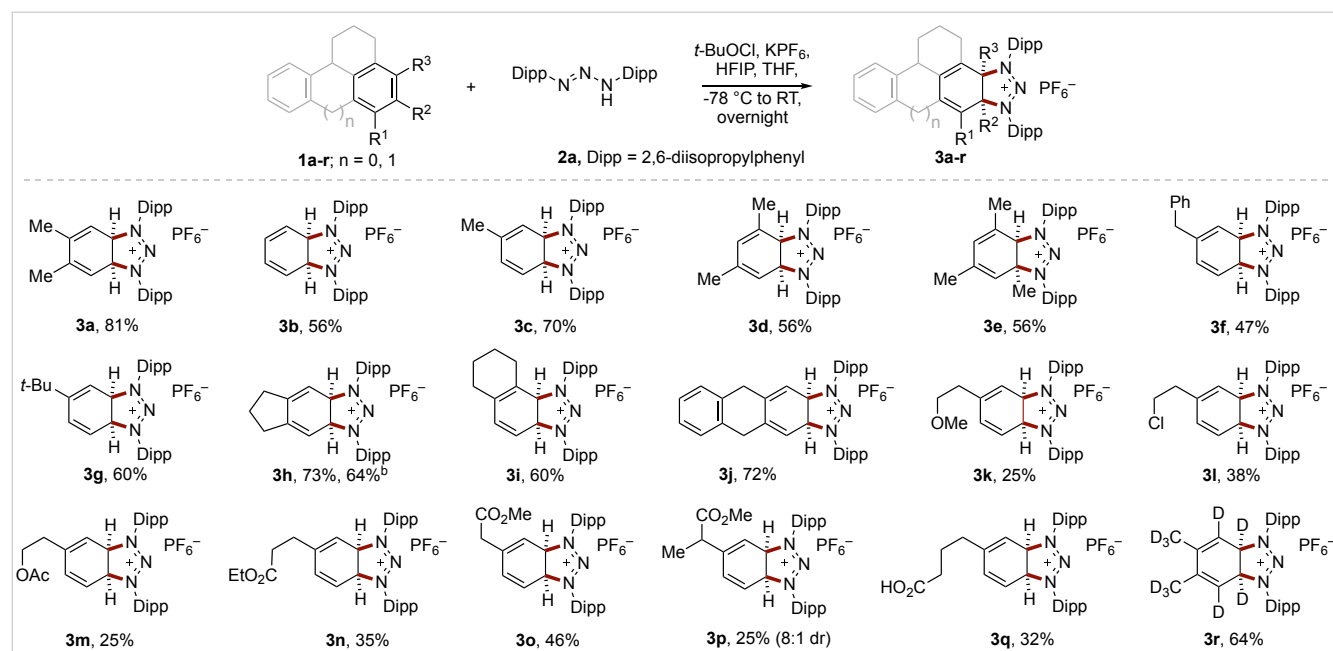
Fluorinated alcohols are known to promote dearomative (4+3) and (3+2) cycloadditions with azaoxallyl²⁹ and diazaoxallyl cations.³⁰ Among these, hexafluoro-2-propanol (HFIP) as an additive successfully raised the yield of **3a** to 81% (entry 6). These were selected as the optimal set of conditions for the preparation of **3a**. Preparation of the adduct **3a** was readily amenable to a multi-gram reaction scale under these optimized conditions affording **3a** in 66% yield (entry 10). In a laboratory setup, the reaction was most easily carried out by allowing a stirred reaction mixture immersed in a dry ice-acetone bath (-78°C) to slowly warm to room temperature. Cryogenic conditions are not necessary, however, and comparable yields were obtained at initial temperatures up to ca. -30°C. Nevertheless, further raising the initial temperature significantly lowered the yields (entries 7-9).

Preliminary calculations performed at the ω B97X-D/def2-TZVP/CPCM(THF) level of theory on the truncated model cycloaddition between benzene (**1b**) and 1,3-bis(2,6-dimethylphenyl)-DAAA⁺ allowed for the identification of a low energy ($\Delta G^\ddagger = 20.2$ kcal/mol) concerted but asynchronous transition state connecting, as confirmed by IRC calculations, the reactants to the dearomatized adduct ($\Delta G = -20.1$ kcal/mol; Figure S4). Comparable results were also obtained using the M06-2X-D3 functional (see the SI for details). These results are consistent with the isolation of thermally stable adducts obtained from the cycloaddition at low temperatures (-78°C to RT) between DAAA⁺ generated *in situ* and arenes.

Some features of the formal (3+2) cycloaddition between DAAA⁺ **II** and arenes distinguish it from previously reported aminative cycloadditions of arenes or heteroarenes.³¹ Though azaoxallyl and diazaoxallyl cations undergo (3+2) or (4+3) cycloadditions with less aromatic heteroarenes such as furans or indoles,^{29,30} no such reactions with monocyclic aromatic hydrocarbons have been reported. The **Scheme 2. Synthesis of triazololinium adducts via a dearomative (3+2) cycloaddition.**^a

cycloaddition of DAAA⁺ **II** is also distinct from the photocycloadditions of TADs, which favor a (4+2) mode as excited-state arenophiles, whereas formal (3+2) adducts were exclusively observed with **II**. Moreover, though the TAD cycloadducts of monocyclic aromatic hydrocarbons are thermally unstable ($t_{1/2} \sim 1$ hr at 0°C for the MTAD-PhH adduct),^{12b} the fused triazololinium adducts **3** remained unchanged at room temperature for tens of hours in solution, days in the solid-state, and could be stored for months in a refrigerator without degradation. The reactivity of DAAA⁺ **II** also contrasts with the closely related 1-aza-2-azoniaallene cations, which were reported by the Brewer group to participate instead in Friedel-Crafts-type alkylations.^{32,33}

The scope of the developed cycloaddition was subsequently studied under the reaction conditions optimized for *o*-xylene, as shown in Scheme 2. Numerous commodity arenes, such as benzene, toluene, and *m*-xylene were found to participate in the cycloaddition leading to the adducts **3b-d**. The yields and regioselectivity indicated a preference for more sterically accessible and electron-rich positions. Cycloaddition was also possible at substituted positions, such as for mesitylene, giving **3e**, but did not take place with hexamethylbenzene. Sterically demanding substituents did not negatively affect the outcome of the reaction (**3g**), but lower yields were observed for some arene substrates bearing branched side chains, possibly due to side reactions occurring at benzylic and/or methine positions. Fused arenes gave high cycloadduct yields, though a switch in the regioselectivity from the indane adduct **3h** to the tetralin adduct **3i** was observed.³⁴ Interestingly, the regioselectivity was reverted to the 2,3-positions in the case of the 9,10-dihydroanthracene adduct **3j**. Even in the presence of an excess of triazene and oxidant, 2:1 adducts were not observed under these conditions; double adducts were not formed with the bisarene substrates **1f** and **1j** either.

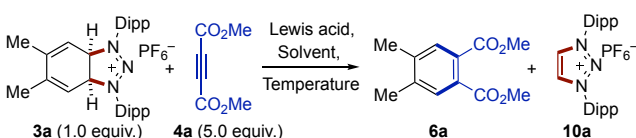


^a Isolated yields. Conditions: **1** (500 μ L), **2a** (1 mmol), *t*-BuOCl (1.1 mmol), KPF₆ (1.1 mmol), HFIP (1.0 mmol) and THF (4.5 mL).
^b Using **1** (1.5 mmol), **2a** (1.5 mmol), *t*-BuOCl (1.5 mmol), KPF₆ (1.65 mmol), HFIP (1.5 mmol) and THF (1.5 mL).

The cycloaddition notably was tolerant of ethers (**3k**), halides (**3l**) and esters (**3m-p**) and carboxylic acids (**3q**). Cycloaddition with *o*-xylene- d_{10} similarly furnished the corresponding deuterated cycloadduct **3r**. The bis(2,6-diisopropylphenyl)triazene **2a** was the sole triazene among those surveyed that accomplished the cycloaddition with monocyclic arenes under these conditions (Scheme S1).

Synthetic applications for the preparation of fused and substituted arenes through a (4+2) Cycloaddition-cycloreversion sequence. The dearomative cycloaddition of arenes with DAAA⁺ **II** activates them toward further synthetic transformations. We hypothesized that the cyclohexadiene subunit within **3** would react with suitable dienophiles **4** to give transient (4+2) cycloadducts **5** (Scheme 1c). The latter were expected to undergo cycloreversions leading to the formation of new arenes (**6**, **8** and **9**) and triazoliums **10** products. The cycloaddition-cycloreversion cascade using the dearomatized triazolium adducts would thus enable the preparation of substituted and fused arenes. The validity of the proposed sequence was first assessed with dimethyl acetylenedicarboxylate (DMAD) **4a**. Consistent with this proposition, upon stirring in acetonitrile at 40 °C for 35 h, a mixture of **3a** and **4a** was found to deliver the expected 4,5-dimethylphthalate **6a** in 61% yield together with the triazolium salt **10a** as byproduct (Table 2, entry 1). Optimization of reaction parameters for the cycloaddition-cycloreversion cascade between the *o*-xylene-derived adduct **3a** and DMAD **4a** revealed that the addition of the mild Lewis acid indium(III) chloride hydrate improved the isolated yield and reaction kinetics, and acetonitrile proved to be the preferred solvent.

Table 2. Optimization study for cycloaddition-cycloreversion cascade of **3a with **4a****



Entry	Solvent	Lewis Acid	Temperature	Yield ^c (%), 6a
1	CH ₃ CN	–	40 °C	61%
2	DCM	ZnCl ₂	RT–40 °C	42%
3	DCM	TiCl ₄	RT–40 °C	15%
4	DCM	EtAlCl ₂	RT–40 °C	trace
5	DCM	LiClO ₄	40 °C	9%
6	CH ₃ CN	LiClO ₄	40 °C	80%
7	CH ₃ CN	InCl ₃ ·4H ₂ O	40 °C	83%
8 ^b	CH ₃ CN	InCl ₃ ·4H ₂ O	40 °C	77%
9	CHCl ₃	InCl ₃ ·4H ₂ O	40 °C	17%
10	DCE	InCl ₃ ·4H ₂ O	40 °C	50%
11	Acetone	InCl ₃ ·4H ₂ O	40 °C	44%

^aReaction conditions: **3a** (0.16 mmol), **4a** (0.8 mmol), Lewis acid (20 mol%) and 1–2 mL of solvent. ^bThe reaction was performed with 10 mol% of InCl₃·4H₂O. ^cIsolated yields.

The reactivity of the dearomatized triazolium adducts **3** is reminiscent, with some distinguishing features, of that of cyclopentadienones, *ortho*-benzoquinones,³⁵ thiophene 1-oxides and 1,1-dioxides,³⁶ 2-pyrones,³⁷ or electron-poor

nitrogen heterocycles³⁸ that undergo (4+2) cycloadditions to yield transient intermediates that rearomatize upon the extrusion of a stable small molecule.³⁹ In comparison to 2-pyrones, substituted derivatives of **3** are obtained in a single step through this dearomative cycloaddition, obviating the need for lengthy synthetic sequences. Furthermore, the triazolium adducts **3** also engage alkynes such as DMAD **4a** at temperatures lower than that required for 2-pyrones (typically > 100 °C), which may be ascribed to the aromatic character of the pyrone but its absence in the triazolium adducts **3**.

Under the above conditions, various dearomatized triazolium adducts **3** readily reacted with electron-deficient alkynes including DMAD **4a**, diphenylbutynedione **4b**, methyl 4-oxo-4-phenylbutynoate **4c** and the sulfonyl propiolates **4d-e** to provide the corresponding substituted arenes in 47–90% yields, as shown with the 17 examples of in Scheme 3a. Oxidation of the substituted dihydroanthracenes with DDQ was facile, providing rapid access to the corresponding acene **7a** in 85% yield (Scheme 3b).

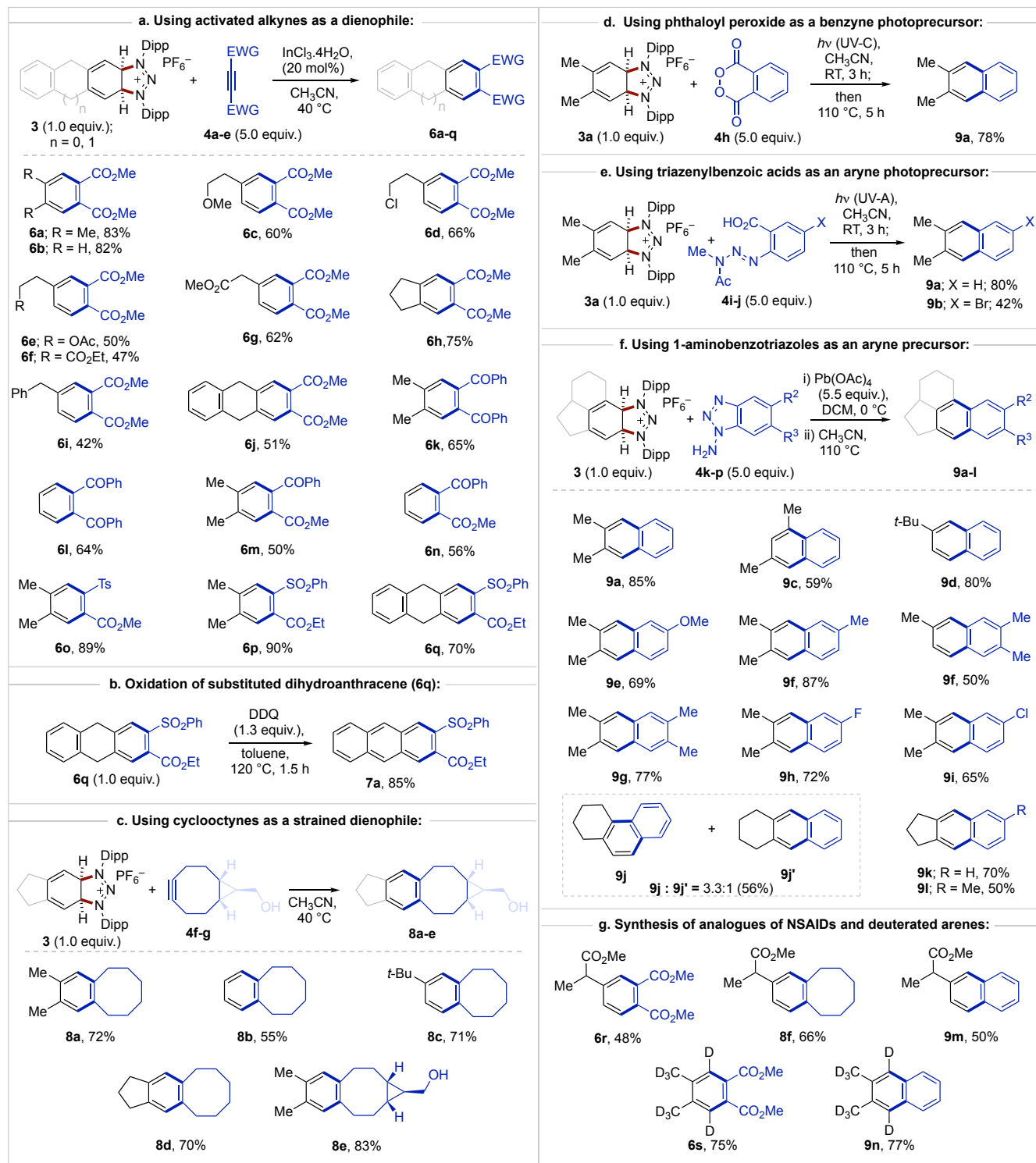
Cyclic alkynes also engaged the dearomatized adducts **3**, providing access to benzo-fused cycloalkanes. Cyclooctyne **4f** and *exo*-BCN **4g**, which exhibit enhanced reactivity as dienophiles owing to their ring strain,⁴⁰ furnished the benzo-fused cycloalkanes **8a-e** in 55–83% yields upon reaction with the adducts **3a**, **3b**, **3g**, and **3h** in CH₃CN at 40 °C (Scheme 3c).

To broaden the scope of fused arenes accessible through the cycloaddition-cycloreversion sequence, arynes were explored as dienophiles.⁴¹ These were found to effect, in combination with the dearomative cycloaddition, the overall excision of a two-carbon fragment and its replacement with a grafted arylene, thereby providing an original disconnection for the synthesis of substituted naphthalenes. Three different types of arylene precursors were found to be suitable for the cycloaddition-cycloreversion cascade with the dearomatized triazolium adducts **3**. First, phthaloyl peroxide **4h** was employed as a benzyne photoprecursor through the loss of CO₂ under UV-C light irradiation.⁴² When a mixture of **3a** and **4h** in CH₃CN was irradiated with a mercury lamp (254 nm), **3a** underwent the targeted (4+2) cycloaddition-cycloreversion cascade with the benzyne intermediate generated *in-situ* to deliver 2,3-dimethylnaphthalene **9a** (Scheme 3d).

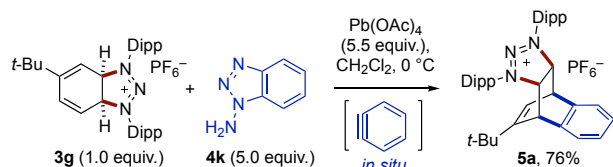
A second photochemical benzyne precursor, the diazonium carboxylate derivative **4i**,⁴³ was also successfully employed, furnishing **9a** in 80% yield through the same sequence (Scheme 3e). This photoprecursor, which releases benzyne with the concomitant loss of CO₂, N₂ and *N*-methylacetamide, has the additional advantage of only requiring milder UV-A (365 nm) light irradiation. A brominated naphthalene derivative **9b** was similarly obtained from deeper UV-sensitive brominated precursor **4j**.

The third compatible way of generating arynes in the cycloaddition-cycloreversion sequence with **3** was the classical oxidation of 1-aminobenzotriazoles (**4k-p**).⁴⁴ Carrying this reaction step at 0 °C enabled the isolation and characterization of the intermediate (4 + 2) cycloadduct **5a** in 76% yield from the reaction between **3g** and **4k**, as delineated in Scheme 4. The isolation of this intermediate **5a** further supports the mechanistic proposal presented in Scheme 1c.

Scheme 3. (a-g) Synthesis of diverse arenes from the dearomatized cycloadducts **3 with dienophiles **4** through a cycloaddition–cycloreversion sequence.**



Scheme 4. Isolation of the transient (4 + 2) adduct **5a.**



For most transformations, the crude **5** was immediately subjected to the (4 + 2) cycloreversion at 110 °C in CH₃CN (Scheme 3f). The above reaction conditions were employed to explore the scope of this transformation with various arene-DAAA⁺ adducts (**3**) and 1-aminobenzotriazoles (**4k-p**), as outlined in Scheme 3f. The protocol was successful for the preparation of substituted naphthalenes (**9a, 9c-l**) in 50-87% yields. Electron-donating and withdrawing

substituents on both the dearomatized adducts and the 1-aminobenzotriazoles were tolerated, and even the bulky *tert*-butyl substituent of **3g** did not diminish the isolated yield of 80% for **9d**. Unexpectedly, subjecting the tetralin adduct (**3i**) to 1-aminobenzotriazole (**4k**) in this cycloaddition-cycloreversion sequence led to formation of a 3.3:1 isomeric mixture of 1,2,3,4-tetrahydrophenanthrene (**9j**) and 1,2,3,4-tetrahydroanthracene (**9j'**). This observation suggests that an isomerization of the unsymmetrical tetralin adduct (**3i**) to its symmetrical isomer (**3i'**) reversibly occurred in solution prior to the cycloaddition step (Scheme S2). However, the indane adduct (**3h**) exclusively gave the expected cyclopentanaphthalenes **9k** and **9l** upon reaction with 1-aminobenzotriazoles **4k** and **4m**, respectively.

The cycloaddition-cycloreversion sequence follows a 2-carbon editing logic⁴⁵ with potential applications in the biomedical sciences. For example, carrying out the cycloaddition-cycloreversion sequence with the DAAA⁺ adduct **3p**, derived from the parent 2-phenylpropanoate **1p**, and different dienophiles offered an unexploited route to diversified analogues of the profen family of non-steroidal anti-inflammatory drugs (NSAIDs, Scheme 3g, **6r**, **8f** and **9m**). Moreover, owing to the widespread availability of deuterated arenes, notably as NMR solvents, the dearomatization-initiated cycloaddition-cycloreversion sequence enabled new paths toward the preparation of selectively isotopically labeled substituted benzenes and naphthalenes (Scheme 3g, **6s** and **9n**).⁴⁶

Current limitations. At this stage of development, the dearomative cycloaddition of arenes and subsequent (4+2) cycloaddition-cycloreversion cascade features some limitations that need to be noted. Though the dearomative cycloaddition was compatible with several polar functional groups, and tolerant of steric hindrance, it was, however, highly sensitive to the electronic character of the arene (Scheme S1). As earlier observed for the (4+2) cycloaddition with TADs,¹³ neither highly electron-poor arenes, which did not engage with the DAAA⁺ **II**, nor highly electron-rich arenes, which gave intractable mixtures of products, were suitable reaction partners under the conditions originally optimized for *o*-xylene. Reactions with commodity arenes gave higher yields when used in excess as co-solvents, as previously reported for TAD photocycloadditions.¹³ Preparatively useful reactions were nevertheless achieved with equimolar amounts of triazene **2a** and arene substrate **3**, at the expense of additional substrate-specific re-optimizations of the reaction conditions (*cf.* **3h**, Scheme 2).

The reactivity of **3** in its (4+2) cycloadditions was restricted to potent dienophiles, though further opportunities for catalysis abound. It was moreover limited by the stability of the triazolium adducts **3**. These formal (3+2) adducts were stable at room temperature, but nevertheless underwent rearomatization through a ring-opening elimination in solution at temperatures greater than ca. 50°C. Therefore, only dienophiles that outcompeted this side reaction were successful in the cycloaddition-cycloreversion sequence. The ring-opening elimination and rearomatization of **3** was also promoted by Brønsted bases as mild as carboxylate anions. For this reason, some versatile methods for the preparation of arynes, such as the activation of Kobayashi's *o*-silyl triflates with fluoride,^{41b,47} or the thermolysis of diazonium carboxylates⁴⁸ were incompatible with

the current conditions for the cycloaddition-cycloreversion sequence. Finally, alkyl substituents at the bridgehead of the triazolium adduct (e.g., **3e**) impeded the approach of the dienophile on one face of the cyclohexadiene ring, while the bulky diaryltriazolium ring thoroughly shielded the opposite face. Consequently, these substrates were inert toward the dienophiles discussed herein in the cycloaddition-cycloreversion cascade.

Notwithstanding these limitations, the combined application of the dearomative cycloaddition and subsequent cycloaddition-cycloreversion cascade has provided an unprecedented disconnection enabling the synthesis, in only two steps, of the substituted and fused arenes shown in Scheme 3; among these, half had never been reported, despite their apparent structural simplicity.

CONCLUSION

The shared understanding that benzene rings will not undergo cycloaddition under ordinary reaction conditions may have beguiled chemists into overlooking synthetically appealing transformations. We here reported that 1,3-diazaazoniaallene cations, which have been known for a quarter-century as remarkably potent in their cycloadditions with various dipolarophiles, can also readily undergo, below 0°C under suitable conditions, formal (3+2) cycloadditions with benzene and its derivatives to yield crystalline thermally stable adducts. This dearomative cycloaddition activates the ring for further synthetic elaboration. As demonstrated herein, it enabled a cycloaddition-cycloreversion cascade with alkynes or arynes that together effect the overall excision of a 2-carbon fragment from the aromatic ring and its replacement with a subrogate fragment from the incoming dienophile, following a skeletal editing logic. We anticipate that the dearomatized triazolium adducts may be enrolled as linchpins in a series of additional transformations, from their cycloadditions to heterodienophiles^{39b} to their reductive ring-cleavage,^{28a} that will find applications in polymer chemistry, the synthesis of functional conjugated organic materials, as well as the preparation of biologically active molecules.

ASSOCIATED CONTENT

Supporting Information.

Experimental procedures and characterization data for novel compounds, computational details including coordinates (PDF).

Accession Codes. CCDC 2240714 (**3a**) and 2242579 (**5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*bouffard@ewha.ac.kr

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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