

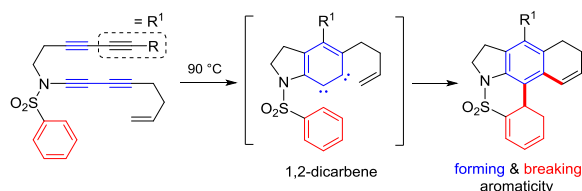
# Reactivity of Arynes for Arene Dearomatization

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Supporting Information Placeholder



**ABSTRACT:** An unprecedented aryne-mediated dearomatization reaction is described. An aryne intermediate generated from arenesulfonyl ynamide-tethered tri- and tetraynes reacts with both the  $\pi$ -systems of a tethered alkene and the arenesulfonyl group to generate cyclohexa-1,3-diene-containing penta- and hexacyclic frameworks. DFT-calculations show a nucleophilic dearomatization mechanism involving a zwitterionic intermediate derived from an aryne. A novel halogen effect on the efficiency of the dearomatization and deterrence of aromatization of the cyclohexa-1,3-diene moiety was also observed.

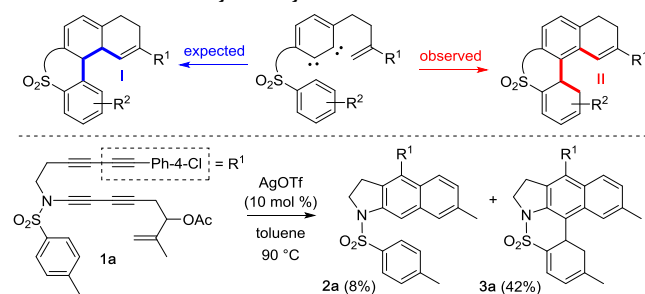
The reactivity of arynes is generally manifested as a strained alkyne, 1,2-diradical, or 1,2-zwitterion depending on the reacting counterpart.<sup>1</sup> In the presence of  $\pi$ -philic transition metals, arynes participate in C–H insertion, which is an evidence for the involvement of 1,2-dicarbene.<sup>2</sup> Although arynes can potentially behave as a 1,2-dicarbene, this reactivity has never been revealed in any aryne-mediated transformations. The arene-dearomatization reactions described herein is the first evidence that the aryne species can interact with two  $\pi$ -systems through free 1,2-dicarbene reactivity.<sup>3</sup>

Dearomatization of arenes to cyclohexa-1,3- or -1,4-dienes could be achieved under a variety of conditions.<sup>4</sup> Among these, breaking aromaticity by adding a nucleophile onto arenes is limited to only a small range of arene structures.<sup>4b–f</sup> Different from polycyclic arenes,<sup>5</sup> monocyclic arenes react only under harsh conditions, resulting in low yield<sup>4f,6</sup> unless complexed with certain transition metals.<sup>4q,4s,7</sup> In this regard, the facile dearomatization of benzene via Diels-Alder reaction with aryne is unique,<sup>8</sup> wherein the relief of strain energy of arynes<sup>9</sup> should play a crucial role.

In the light of the previously reported Ag(I)-catalyzed C–H insertion reaction,<sup>2</sup> we surmised that under appropriate environment the 1,2-dicarbene can participate in two independent C( $sp^2$ )–H insertion events (Scheme 1). When **1a** was subjected to a typical conditions

(10 mol % AgOTf, toluene, 90 °C),<sup>10</sup> two products **2a** and **3a** were obtained.<sup>11</sup> While **2a** is the result of a mono C–H insertion followed by elimination of AcOH, the product **3a** can be considered as the result of an unprecedented 1,2-dicarbene mechanism.

Scheme 1. Discovery of Aryne-mediated Dearomatization



Based on the formation of novel multicyclic framework involving arene dearomatization, we further explored the scope of this transformation. First, we tried to optimize the reaction conditions along with the variation in the structure of the tethered alkene (Table 1). It was found that AgOTf did not have a noticeable effect on the reaction, and PhCF<sub>3</sub> was the most favorable solvent (entry 1). The substituent on the alkene tether, for example, *p*-nitrophenylcarboxy and pivaloxy group at the allylic position has almost no effect on yields (entry 2 vs 3).

Relocating the oxygen substituent from the allylic to the propargylic position did not affect the yield (entry 4 vs 5). Free hydroxyl group such as in **1f** did not interfere with the reaction,<sup>12</sup> affording **3e** in comparable yield (entry 6). Substrate **1g** containing a styryl moiety produced hexacyclic product **3g** (entry 7), whereas a similar substrate **1h** afforded product **4h** and **2h** in 40 and 18% yield (entry 8).

At this juncture, we surmised that the yield of the reaction could be improved by circumventing the elimination process, thus, we explored the reactivity of tetraynes

Table 1. Optimization and the Effect of an Alkene Tether

| entry | substrate                                  | conditions <sup>a</sup> | product                      | yield (%) <sup>b</sup> |
|-------|--|-------------------------|------------------------------|------------------------|
| 1     | <b>1a</b> , R = Ac                         | A                       | <b>3a</b>                    | 42 <sup>c</sup>        |
| 2     | <b>1b</b> , R = 4-NO <sub>2</sub> -Benzoyl | A                       | <b>3a</b>                    | 35 <sup>c</sup>        |
|       |  | C                       | <b>3a</b>                    | 44 <sup>c</sup>        |
|       |  | A                       | <b>3a</b>                    | 47 <sup>d</sup>        |
| 3     | <b>1c</b> , R' = Piv, R = Me               | A                       | <b>3c</b> , R = Me           | 45                     |
| 4     | <b>1d</b> , R' = Ac, R = H                 | A                       | <b>3d</b> , R = H            | 40 <sup>e</sup>        |
| 5     | <b>1e</b> , R =                            | C                       | <b>3e</b>                    | 40                     |
| 6     | Ac   | C                       | <b>3e</b>                    | 41                     |
|       | <b>1f</b> , R = H                          |                         |                              |                        |
| 7     | <b>1g</b> , R = H, R' = H                  | B                       | <b>3g</b> , R = H, R' = H    | 36                     |
| 8     | <b>1h</b> , R = Me, R' = OMe               | C                       | <b>3h</b> , R = Me, R' = OMe | 40                     |

<sup>a</sup>Conditions: A = AgOTf (10 mol %), PhCH<sub>3</sub>, 90 °C; B = PhCH<sub>3</sub>, 90 °C; C = PhCF<sub>3</sub>, 90 °C. <sup>b</sup>Isolated yield. <sup>c</sup>Yield from **1a**. <sup>d</sup>Yield from **1b**. <sup>e</sup>In PhCl and 1,2-dichloroethane, **3d** was obtained in 34 and 40% yield, respectively.

devoid of an oxygen substituent (Table 2). Tetrayne **1i** containing a carboxylate in the tether afforded **4i** with a 1.3:1 diastereomeric ratio (entry 1). Tetrayne **1j** containing an allyldimethylsilyl group afforded silacyclic product **4j** in 35% yield (entry 2).<sup>13</sup> Although not involving the elimination step, the yield of **4i** and **4j** still remained in a marginal range. A significant increase in yield was achieved by installing a vinyl bromide moiety in tetrayne **1k**, which yielded **4k** in 67% yield (entry 3). Encouraged by this result, the impact of different halogen substituents on the efficiency of the reaction was examined. From tetraynes **1l–1o** differing only by the halogen substituent on the alkene moiety, pentacyclic product **4l–4o** were obtained in good yield (entries 4–7). One noteworthy observation is that the elimination of AcOH is shunted in these products containing a haloalkene moiety. The highest yield with **1l** bearing a fluoride-substituent might

be the consequence of the carbocation-stabilizing effect of the fluoride with an intermediate along the reaction path.<sup>14</sup>

Next, we explored the impact of electron-donating and withdrawing substituents on the arenesulfonamide (Table 3). The reaction of **1p** containing a 4-MeOPh afforded only 37% yield of **3p** (entry 1) whereas **1q** with a phenyl group provided **3q** in 48% yield (entry 2). Substrate **1r** with a phenyl instead of a methyl group on the alkene afforded **3r** in 46% yield (entry 3). The 4-fluoro and 4-trifluoromethyl group in **1s** and **1t** slightly improved the yield, providing **4r–4t** in 53 and 59% yields (entries 4 and 5). These examples clearly suggest more electron-deficient arenesulfonyl group can improve the yield. Substrate **1u** with 3-CF<sub>3</sub> afforded **3u** in 51% yield (entry 6) while **1o** with a 3,5-difluorophenyl group provided **3v** in 35% yield (entry 7). Naphthalene-2-sulfonyl substrate **1w** furnished a 1:2.3 mixture of **3w'** and **3w** in 53% yield (entry 8).

Table 2. Effect of the Substituents on the Alkene

| entry | substrate          | conditions <sup>a</sup> | product                              | yield (%) <sup>b</sup> |
|-------|--------------------|-------------------------|--------------------------------------|------------------------|
| 1     | <b>1i</b>          | B                       | <b>4i</b><br>dr = 1.3:1 <sup>c</sup> | 38                     |
| 2     | <b>1j</b>          | C                       | <b>4j</b><br>X-ray                   | 35 <sup>d</sup>        |
| 3     | <b>1k</b>          | C                       | <b>4k</b><br>dr = 1:1 <sup>c</sup>   | 67                     |
| 4     | <b>1l</b> , X = F  | C                       | <b>4l</b> , X = F                    | 72                     |
| 5     | <b>1m</b> , X = Cl | C                       | <b>4m</b> , X = Cl                   | 61                     |
| 6     | <b>1n</b> , X = Br | C                       | <b>4n</b> , X = Br                   | 63                     |
| 7     | <b>1o</b> , X = I  | C                       | <b>4o</b> , X = I                    | 67                     |

<sup>a</sup>Conditions: B = PhCH<sub>3</sub>, 90 °C; C = PhCF<sub>3</sub>, 90 °C. <sup>b</sup>Isolated yield. <sup>c</sup>Mixture of diastereomers. <sup>d</sup>Slightly higher 43% yield was obtained with a phenyl instead of a tolyl group.

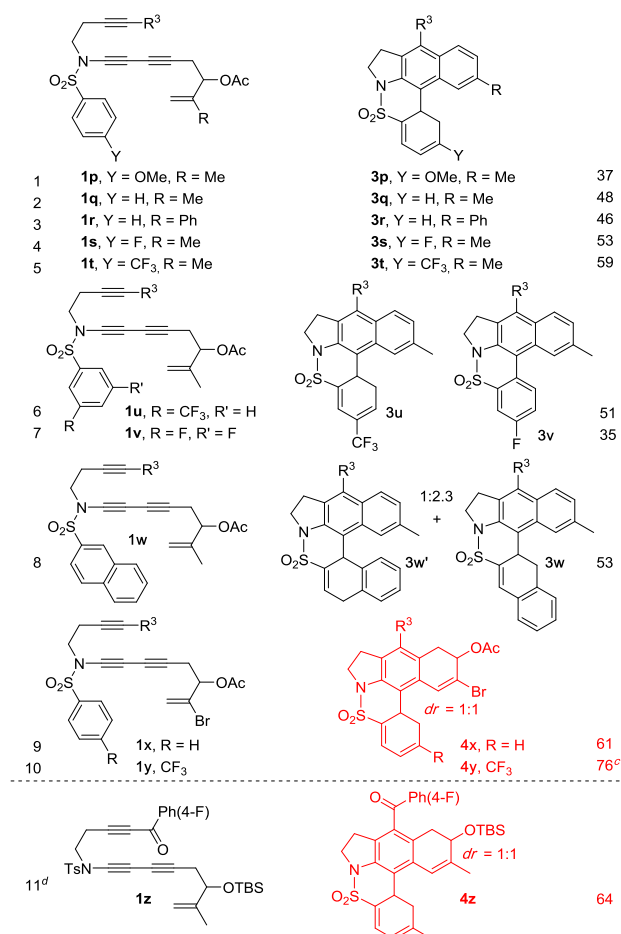
Comparison of **1x** and **1y** containing a vinyl bromide clearly shows the beneficial effect of an electron-withdrawing 4-CF<sub>3</sub> on the arenesulfonyl moiety, providing 61 and 76% yield of **4x** and **4y**, respectively (entries 9 and 10). The dearomatization occurred with the aryne intermediate generated from ketone-containing triyne **1z** providing **4z** at slightly higher temperature, where the silyl ether remained unreacted.<sup>10e</sup>

The mechanism of this unprecedented aryne-mediated dearomatization process was explored by DFT

calculation<sup>15</sup> employing a structurally simplified aryne **IN1** (Scheme 2). The calculated lowest energy pathway reveals a 1,2-dicarbene character of **IN2** through aryne, which promotes the concerted formation of a cyclopropyl carbene via a relatively low energy transition state **TS1**. Carbene **IN2** behaves like a zwitterion such that it undergoes nucleophilic addition (**Path I**) onto an electron-deficient arenesulfonyl group via **TS2** to generate 1,3-zwitterion **IN3**. The ring expansion of the cyclopropyl moiety of **IN3** generates isomeric 1,6-zwitterion **IN4**, which leads to the final product **P** via **TS4** for intramolecular proton transfer. The change of  $\Delta G$  going from aryne **IN1** to product **P** is  $-58.7$  kcal/mol and the highest barrier involved in the dearomatization is only  $14.8$  kcal/mol, thus this overall process should be kinetically and thermodynamically favorable. On the other hand, the energy of **TS6** leading to product **P-2** (**Path II**) is  $10.9$  kcal/mol higher than that of **TS2** leading to product **P-3/4**. Also, the unusual stability of the vinyl halide-containing products such as **41-40** toward aromatization was computationally studied. The DFT-calculations with **Model-4** show that a fluoro-substituent raises the activation barrier for the AcOH elimination. Even though the calculations corroborate experimental observations, the reason for this unusual phenomenon is yet to be identified.

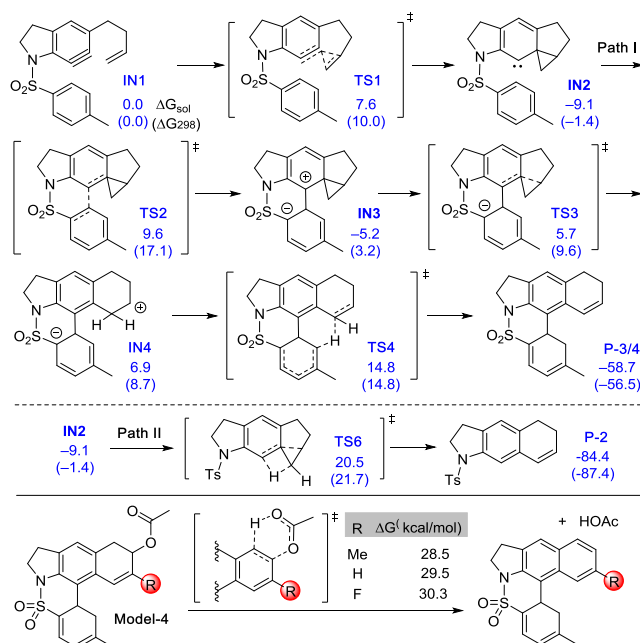
Table 3. Effect of the Substituents on the Arenesulfonamide

| entry | substrate | product <sup>a</sup> | yield (%) <sup>b</sup> |
|-------|-----------|----------------------|------------------------|
|-------|-----------|----------------------|------------------------|

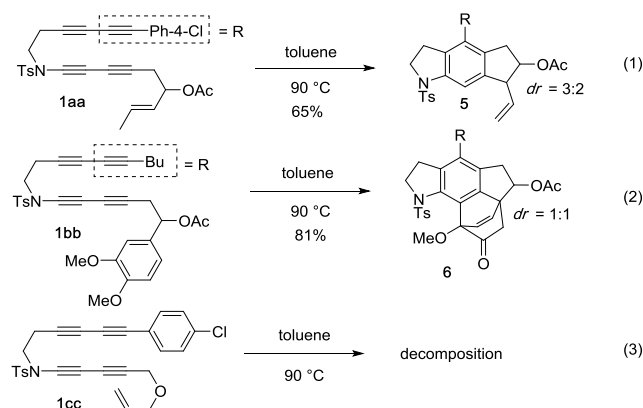


<sup>a</sup>PhCF<sub>3</sub>, 90 °C. <sup>b</sup>Isolated yield. <sup>c</sup>In a 1.0 gram-scale reaction, **4y** was isolated in 67% yield. <sup>d</sup>PhCF<sub>3</sub>, 120 °C.

Scheme 2. DFT-based Mechanistic Study [ $\Delta G_{\text{sol}}$  and  $\Delta G_{298}$  are relative free energies (kcal/mol) calculated in solution and in gas phase, respectively]



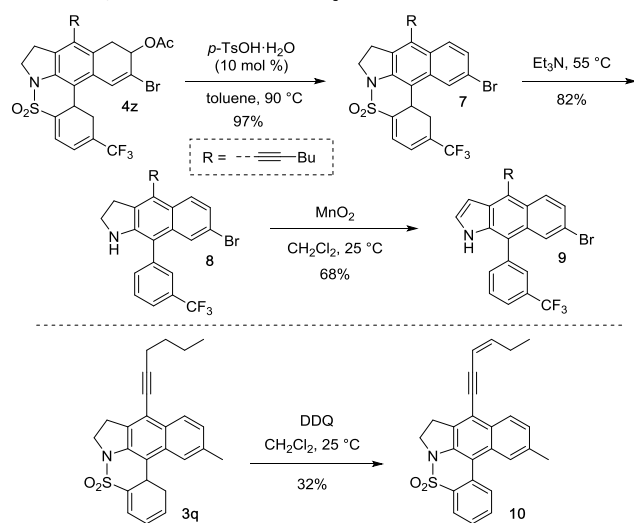
Scheme 3. Substrates with an Unsuitable Alkene Moiety



A limitation was noticed regarding the alkene structure on tetrayne substrates (Scheme 3). A non-terminal alkene in **1aa** favorably participates in a type-I Alder-ene reaction, generating **8** (eq 1). The electron-rich aromatic  $\pi$ -system in **1bb** led to only Diels-Alder reaction,<sup>16</sup> forming benzobarrelene **9** after hydrolysis (eq 2), whereas allyl ether-tethered tetrayne **1cc** just decomposed (eq 3). These results indicate that a terminal alkene tethered with a two-atom tether to the aryne moiety is required for dearomatization reaction.

The reactivity of a representative dearomatized compound **4z** was explored (Scheme 4). Treatment of **4z** with *p*-TsOH·H<sub>2</sub>O (10 mol %) at 90 °C induced aromatization via elimination of AcOH, affording compound **7**. The sulfonamide of **7** could be removed easily by treating **7** in Et<sub>3</sub>N at 55 °C, providing compound **8**, which is the consequence of a base-mediated alkene isomerization and an E2-type elimination. The indoline moiety in **8** was oxidized by MnO<sub>2</sub> to generate a unique 1*H*-benzo[*f*]indole containing biaryl structure **9**. In contrast, oxidation of **3q** with DDQ afforded **10** with intact indoline moiety in low yield.

Scheme 4. Chemical Reactivity of Dearomatized Products



In conclusion, we discovered a novel dearomatization reaction mediated by the 1,2-dicarbene reactivity of arynes. In this process, one aromatic system is generated

via HDDA reaction as a form of an aryne, the high reactivity of which then ensues the dearomatization of the tethered aryl group connected through a sulfonamide linkage. The efficiency of this transformation is profoundly affected by substrate structures, where a cation-stabilizing substituent on the tethered alkene and electron-withdrawing substituents on the arenesulfonyl group increased the efficiency of the reaction. DFT-calculations revealed that the 1,2-dicarbene character of an aryne promoted cyclopropanation with the nearby alkene followed by a nucleophilic attack of the remaining carbene as a form of zwitterion onto the electron-deficient arenesulfonyl group, leading to dearomatization after proton shift in the final step. The relatively strained pentacyclic framework can be readily converted to a useful building blocks including 1*H*-benzo[*f*]indole containing a CF<sub>3</sub> group.

## ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and characterization data. The Supporting Information is available free of charge on the ACS Publications website.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interests.

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- (13) The structure of **4j** was confirmed by X-ray diffraction analysis (CCDC 1574874). This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
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