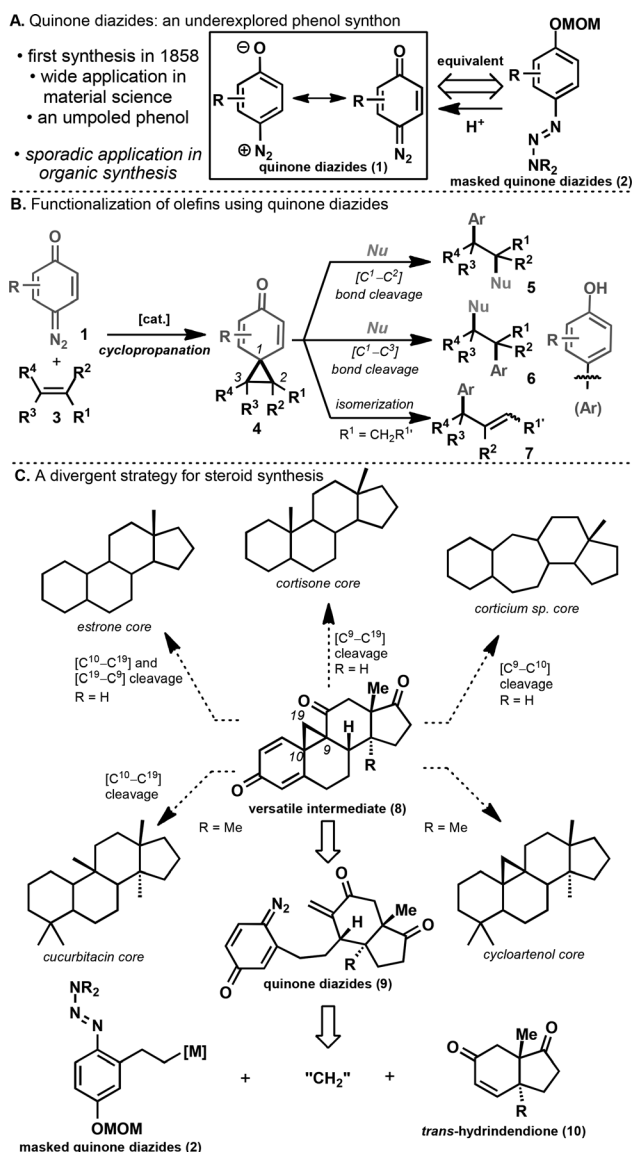


# Quinone Diazides for Olefin Functionalization\*\*

Hai T. Dao and Phil S. Baran\*

**Abstract:** The utility of quinone diazides in materials science is vast and well-documented, yet this potentially useful motif has languished in the annals of organic synthesis. Herein we show that modern tools of catalysis can be employed with free or suitably masked quinone diazides to unleash the power of these classic diazo compounds in the context of both inter- and intramolecular olefin cyclopropanation.

Quinone diazides (or arene diazo oxides; *p*-quinone diazides **1**, Scheme 1A) are among the oldest diazo compounds, with the first documented occurrence in 1858.<sup>[1]</sup> Owing to their high reactivity, a range of applications has emerged in disparate fields such as polymer chemistry,<sup>[2a]</sup> photolithography,<sup>[2b]</sup> photoaffinity labeling,<sup>[2c,d]</sup> and electronic and optical materials.<sup>[2e,f,g]</sup> Typically, they are synthesized by the diazotization of an aminophenol or functionalization of an aniline or phenol; the resulting quinone diazides can be isolated or used in situ.<sup>[1]</sup> The 1960s to 1980s represented a “golden age” of quinone diazide chemistry, with a great focus on azo coupling, thermolysis and photolysis-promoted Wolff-type rearrangements, and decomposition of the diazo moiety to the corresponding cyclohexadienone carbene.<sup>[1a,3]</sup> This final mode of reactivity presents an untapped opportunity for synthesis, since these carbenes render a phenol electrophilic at its normally nucleophilic *para* or *ortho* position. However, a lack of efficient and mild synthetic methods to manipulate quinone diazides likely contributed to the paucity of applications for the construction of complex molecules. Our interest in this underexplored species stemmed from the structurally ornate cyclopropanes that might be generated from their union with olefins (Scheme 1B). These versatile compounds could be either nucleophilically opened or isomerized. Herein, a method for harnessing the reactive carbenes derived from quinone diazides by using modern catalysts to achieve a general catalytic intermolecular functionalization of olefins with these classic species is reported.<sup>[4]</sup> In addition, a simple storage and mild release of quinone diazides in an intramolecular context has enabled a unique divergent approach to steroid synthesis (Scheme 1C).



**Scheme 1.** Quinone diazides and masked quinone diazides in organic synthesis.

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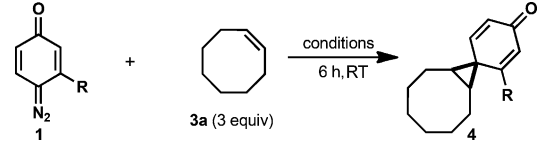
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Quinone diazides can be classified as carbonyl diazo compounds bearing two electron-acceptor groups.<sup>[5,6]</sup> This class of diazo substrates possesses higher stability, thus making them less susceptible toward metal-catalyzed decomposition. Therefore, harsh conditions, such as elevated temperature or reactive catalysts, are often required for the formation of metal carbenoids.<sup>[5a,d,6]</sup> Furthermore, these highly electrophilic carbenoids are prone to side reactions such as carbene dimerization and hydride transfer to form zwitterionic intermediates. In addition to these potential challenges, the resulting cyclopropanes **4** (Scheme 1B) are

prone to undergo C–C cleavage-induced rearomatization. Thus, to promote this two-step olefin functionalization, mild conditions for the cyclopropanation step and selective conditions for the cleavage step are required. With this in mind, optimization was initially focused on the intermolecular cycloaddition of quinone diazide **1a** and cyclooctene **3a** (Table 1). Monosubstituted quinone diazide **1a** was selected

**Table 1:** Optimization of the cyclopropanation of quinone diazides **1** and olefin **3a**.



| Entry             | <b>1</b>           | Cat. (5 mol %)                         | Solvent                         | Conv. [%] <sup>[a]</sup> | Yield [%]         |
|-------------------|--------------------|----------------------------------------|---------------------------------|--------------------------|-------------------|
| 1                 | <b>1a</b> (R = Br) | –                                      | CH <sub>2</sub> Cl <sub>2</sub> | NR                       | –                 |
| 2                 | <b>1a</b> (R = Br) | [Rh <sub>2</sub> (OAc) <sub>4</sub> ]  | CH <sub>2</sub> Cl <sub>2</sub> | < 5                      | –                 |
| 3 <sup>[b]</sup>  | <b>1a</b> (R = Br) | [Rh <sub>2</sub> (OPiv) <sub>4</sub> ] | CH <sub>2</sub> Cl <sub>2</sub> | 40                       | 10                |
| 4                 | <b>1a</b> (R = Br) | [Rh <sub>2</sub> (hfb) <sub>4</sub> ]  | CH <sub>2</sub> Cl <sub>2</sub> | 20                       | 5                 |
| 5                 | <b>1a</b> (R = Br) | [Rh <sub>2</sub> (esp) <sub>2</sub> ]  | CH <sub>2</sub> Cl <sub>2</sub> | full conv                | 35                |
| 6 <sup>[c]</sup>  | <b>1a</b> (R = Br) | [Cu(acac) <sub>2</sub> ]               | CH <sub>2</sub> Cl <sub>2</sub> | NR                       | –                 |
| 7                 | <b>1a</b> (R = Br) | AgSbF <sub>6</sub>                     | CH <sub>2</sub> Cl <sub>2</sub> | NR                       | –                 |
| 8                 | <b>1a</b> (R = Br) | [Rh <sub>2</sub> (esp) <sub>2</sub> ]  | hexanes                         | < 20                     | –                 |
| 9                 | <b>1a</b> (R = Br) | [Rh <sub>2</sub> (esp) <sub>2</sub> ]  | Et <sub>2</sub> O               | < 30                     | –                 |
| 10 <sup>[d]</sup> | <b>1a</b> (R = Br) | [Rh <sub>2</sub> (esp) <sub>2</sub> ]  | benzene                         | full conv                | –                 |
| 11 <sup>[e]</sup> | <b>1a</b> (R = Br) | [Rh <sub>2</sub> (esp) <sub>2</sub> ]  | CH <sub>2</sub> Cl <sub>2</sub> | full conv                | 66 <sup>[f]</sup> |
| 12 <sup>[e]</sup> | <b>1a'</b> (R = H) | [Rh <sub>2</sub> (esp) <sub>2</sub> ]  | CH <sub>2</sub> Cl <sub>2</sub> | full conv                | 44                |

[a] Consumption of **1** determined by <sup>1</sup>H NMR spectroscopic analysis of crude materials. [b] Catalyst decomposed. [c] Stoichiometric loading. [d] Only a by-product resulting from reaction with the solvent was obtained. [e] Molecular sieves (4 Å MS) were used as the additive; slow addition of quinone diazide **1** over 5 h, then additional 4 h at RT. [f] A single diastereomer was obtained. Piv = pivaloyl, esp = α,α,α',α'-tetramethyl-1,3-benzenedipropionate, acac = acetyl acetonate, hfb = heptafluorobutylate, NR = no reaction.

due to its ease of synthesis from the corresponding aminophenol, and the synthetic versatility of the products. In the first experiments, the uncatalyzed reaction between quinone diazide **1a** and cyclooctene (**3a**; 3 equiv) did not occur, and a catalytic amount of [Rh<sub>2</sub>(OAc)<sub>4</sub>] proved to be ineffective (entries 1 and 2). Encouragingly, when the more soluble [Rh<sub>2</sub>(OPiv)<sub>4</sub>] was employed, a substantial amount of decomposition of **1a** was observed, together with a small amount of the desired cyclopropane adduct **4a** (R = Br; entry 3). It is notable that the coupling product between **1a** and pivalate anion was also isolated, thus indicating decomposition of the catalyst. Strikingly, when the more reactive [Rh<sub>2</sub>(hfb)<sub>4</sub>] catalyst was employed, nitrogen extrusion from quinone diazide **1a** was less effective (entry 4 versus entry 3).<sup>[5a]</sup> To our delight, when the more stable [Rh<sub>2</sub>(esp)<sub>2</sub>] was employed, the decomposition of the diazo moiety occurred efficiently with substantial improvement in the yield of the isolated desired coupling adduct **4a** (entry 5 versus entry 4).<sup>[7]</sup> Other metal catalysts, [Cu(acac)<sub>2</sub>] and AgSbF<sub>6</sub>, did not promote the desired reaction under the same conditions even with the use of stoichiometric loading (entries 6 and 7). The use of

CH<sub>2</sub>Cl<sub>2</sub> as solvent and a slow addition procedure, in combination with the use of molecular sieves, improved the yield of the isolated cyclopropanation product (entries 8–11). In addition, under these optimal conditions, unsubstituted quinonediazide **1a'** reacted with **3a** to yield **4a'** (R = H) in good yield (entry 12).

Next, the substrate scope including the proposed selective C–C bond cleavage was investigated (Table 2). Cycloaddition of monosubstituted olefin **3b** under optimized conditions proceeded smoothly even with a lower catalyst loading (2 mol %). Selective C–C bond cleavage was investigated in a one-pot procedure. Thus, immediately after the cyclopropanation, exposure of the mixture to HCl initiated an S<sub>N</sub>1-type reaction, thereby leading to the formation of **5b** in an excellent yield. This reaction represents a rare example of a direct olefin chloroarylation.<sup>[8]</sup> In another example of unique olefin difunctionalization, the use of a sulfur-based nucleophile on cyclopropane **4b** led to the selective cleavage of the other C–C bond (presumably through an S<sub>N</sub>2-type mechanism) to give **6b** in high yield. As a testament to the versatility of quinone diazide/olefin adducts, formal isomerization of **4b** could be achieved (TMSOTf/Et<sub>3</sub>N) to give unsaturated products **7b** in high yield. Other monosubstituted olefins, including aliphatic bromide **3c**, also participated in the one-pot, two-step sequence to give good yields of the difunctionalized products (**5c** and **5d**). The functionalization of 1,1-disubstituted olefins was investigated with the use of readily available terpenes (**3e–g**). Under optimized conditions, the coupling of these natural products and quinone diazide **1a** proceeded smoothly to yield formal allylic oxidation adducts (**7e–g**). It is thought that in situ formed cyclopropanes (**4e–g**) readily undergo isomerization to these phenolic coupling products. Hetero-substituted olefins such as **3h–j** also resulted in phenolic products (**7h–j**) with good yields under mild conditions. Trisubstituted olefins such as **3j** and **3k** are less reactive under the same reaction conditions, and the more nucleophilic **3j** gave a higher yield than **3k**.

The steroid skeleton was targeted to evaluate the use of quinone diazides in the context of complex molecule synthesis. Steroids are ubiquitous and can be classified on the basis of the structure of various core skeletons: estrane (estrane), cortisone (cholestane, cholane, pregnane, and androstane), corticium sp., cycloartenol, and cucurbitacin (Scheme 1C). A divergent strategy to access different steroid scaffolds by a single pathway is challenging. In this context, intermediate **8** was envisioned to be a versatile precursor to access these different skeletons through selective C–C bond cleavage and isomerization events. Synthesis of this steroid skeleton, potentially accessible from quinone diazide **9**, would require a method to store and generate a quinone diazide moiety under extremely mild conditions. A practical precursor of a quinone diazide that could be both easily installed and unveiled was therefore designed. Since its resonance structure is an oxyaryldiazonium zwitterion (Scheme 1A), it was anticipated that methoxymethyl (MOM) and triazene groups would effectively shield the oxyanion and diazo species, respectively, and be easily unmasked under mildly acidic conditions.<sup>[9]</sup> This masked quinone diazide was anticipated to arise from the union of triazenes **2** with *trans*-bicyclic

**Table 2:** Substrate scope for functionalization of olefin **3b–k** with quinone diazide **1a**.

| Entry <sup>[a]</sup> | Olefins   | Conditions B             | Products | Yield [%]<br>(isomer ratio)                    | Entry <sup>[a]</sup> | Olefins | Conditions B | Products | Yield [%] |
|----------------------|-----------|--------------------------|----------|------------------------------------------------|----------------------|---------|--------------|----------|-----------|
| 1 <sup>[b]</sup>     |           | HCl                      |          | 93<br>(33:1)                                   | 7 <sup>[f]</sup>     |         | none         |          | 57        |
| 2 <sup>[c]</sup>     | <b>3b</b> | EtSH                     |          | 63<br>(3.5:1)                                  | 8 <sup>[f]</sup>     |         | none         |          | 46        |
| 3 <sup>[d]</sup>     | <b>3b</b> | TMSOTf/Et <sub>3</sub> N |          | 79<br>(Δ <sup>1</sup> :Δ <sup>2</sup> = 3.3:1) | 9 <sup>[g,h]</sup>   |         | none         |          | 69        |
| 4 <sup>[b]</sup>     |           | HCl                      |          | 53                                             | 10 <sup>[f,i]</sup>  |         | none         |          | 39        |
| 5 <sup>[e]</sup>     |           | LiCl                     |          | 56                                             | 11 <sup>[g,i]</sup>  |         | none         |          | 48        |
| 6 <sup>[f]</sup>     |           | None                     |          | 67                                             | 12 <sup>[f,i]</sup>  |         | none         |          | 24        |

[a] Conditions A: Slow addition of **1a**, [Rh<sub>2</sub>(esp)<sub>2</sub>] (2–5 mol%), CH<sub>2</sub>Cl<sub>2</sub>, 15–45 °C. Conditions B: [b] HCl (2 equiv), –78 °C to RT. [c] EtSH (25 equiv), –78 °C to RT. [d] TMSOTf (10 equiv), Et<sub>3</sub>N (14 equiv), 0 °C to RT. [e] LiCl, –78 °C to RT. [f] Isomerization occurred during the course of the reaction and/or quenching. [g] Hydrolysis during quenching. [h] 2 equiv of **3h** was used. [i] 1.5 equiv of **3i** and **3j** was used. [j] 5 equiv of **3k** was used.

enones **10** by conjugate addition followed by trapping with a one-carbon electrophile (Scheme 1 C).

The synthesis of triazene **14** commenced from bromophenol derivative **11** (Scheme 2 A). In the event, **11** underwent coupling with trimethylsilylacetylene (TMSA) under standard Sonogashira reaction conditions to afford the desired nitro product in 98 % yield. After reduction of the nitro group, triazene formation was achieved by diazotization of the resulting amine moiety followed by trapping with *i*Pr<sub>2</sub>NH.<sup>[9a]</sup> Removal of the TMS group gave triazene **13** in 69 % yield over 3 steps. Lastly, vinyl iodide **14** was synthesized from alkyne **13** by nickel-catalyzed hydroalumination, followed by in situ trapping with NIS (51 % yield).<sup>[10]</sup>

The precursor to the right-hand side of intermediate **8**, *trans*-hydrindenone **18** was prepared in a concise sequence (Scheme 2 B) inspired by past successes to access such scaffolds from the Denmark as well as Nakamura and Kuwajima research groups.<sup>[11]</sup> Thus, copper-catalyzed conjugate addition of vinylmagnesium bromide to enone **15** followed by trapping with TMSCl was conducted. Allylation of the resulting silyl enol ether was achieved under Tsuji–Trost conditions to give *trans* ketone **16** in high yield (83 %

yield over 2 steps) with high diastereoselectivity (*trans/cis* = 10:1).<sup>[12]</sup> Ketone **16** was then protected with ethylene glycol (86 % yield), followed by ozonolysis of both terminal olefinic moieties to give keto-aldehyde **17** (74 % yield), thereby setting the stage for the key intramolecular aldol reaction step. This aldol condensation is challenging owing to a potential isomerization of the α-hydrogen atom to a thermodynamically more stable *cis* isomer. This issue was overcome by treating **17** with LiOH in *i*PrOH, followed by bromination and elimination, which resulted in a 63 % overall yield of the desired *trans* isomer (6 % yield of *cis* isomer).<sup>[13]</sup>

After extensive screening of different conjugate addition methods to merge vinyl iodide **14** and enone **18** (Scheme 2 C),<sup>[14]</sup> it was discovered that the vinylmagnesium species, derived from magnesium–iodine exchange of vinyl iodide **14** and *i*PrMgCl–LiCl (Knochel's reagent), was ideally suited for this purpose.<sup>[15]</sup> After generation, it underwent copper(I)-catalyzed conjugate addition to enone **18**, followed by trapping with TMSCl to give the corresponding 1,4-adduct in 69 % yield. The olefin moiety of the coupling product was selectively reduced (Pd/C, H<sub>2</sub>) to yield silyl enol ether **19** in quantitative yield. A final carbon atom was added by



intramolecular settings using a triazene-enabled “mask”, and 4) application to a fundamentally different approach to the steroid skeleton.

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