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# Synthesis of Diazonaphthoquinones from Naphthols by Diazo-Transfer Reaction

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Various orthodiazonaphthoquinones (1-diazo-2(1*H*)-naphthalenones and 2-diazo-1(2*H*)-naphthalenones) were synthesized using the diazo-transfer reaction between the appropriate naphthol and 2-azido-1,3-dimethylimidazolinium chloride (ADMC). The ADMC was prepared by the reaction between 2-chloro-1,3-dimethylimidazolinium chloride and sodium azide. The diazo-transfer reaction selectively introduced the diazo group at the C(2) position of 1-naphthol or the C(1) position of 2-naphthol. The naphthalenediols that were tested, except for 1,3-naphthalenediol, also reacted with ADMC to afford the corresponding monodiazotized compound. X-ray analyses suggested that the diazonaphthoquinones did not have diazoniumnaphtholate structures but had diazocarbonyl structures.

Orthodiazonaphthoquinones (1-diazo-2(1*H*)-naphthalenones **1** and 2-diazo-1(2*H*)-naphthalenones **2**, Figure 1) are relatively stable cyclic α-diazocarbonyl compounds,[1] and they are exclusively used as photoresists (e.g., the novolak-diazonaphthoquinone resist).[2] α-Diazocarbonyl compounds are often used in organic syntheses involving carbene and carbenoid intermediates;[3] therefore, it is expected that diazonaphthoquinones could reliably be used as aromatic units for the synthesis of bioactive aromatic natural products and aromatic functional materials through the corresponding carbene or carbenoid intermediates. However, although the Wolff rearrangement of orthodiazonaphthoquinones, which is the key reaction for photoresists, has been widely investigated,[4] the development of other reactions and the application of diazonaphthoquinones as aromatic building blocks are found to be limited,[5] partly because of the difficulties involved in synthesizing diazonaphthoquinones.[1]

In general, orthodiazonaphthoquinones are synthesized from naphthols in several steps. Routes for synthesizing 1-diazonaphthoquinones **1** are shown in Scheme 1, which shows that **1** can be synthesized via aminonaphthols (Route a)[6] or orthoquinones (Route b).[7] Neither of these routes are short, and both require a regioselective transformation, such as amination in Route a and hydrazonation in Route b, to occur. The diazo-transfer reaction involving naphthol is the shortest direct synthetic method (Route c),[3,8] but this method is not commonly used to synthesize diazonaphthoquinones. To the best of our knowledge, 2-azido-3-ethylbenzothiazolium tetrafluoroborate (**3**), synthesized by Balli et al., is the reagent with which

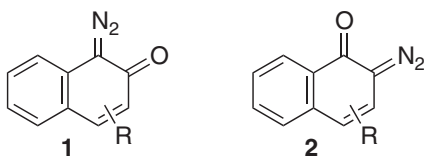
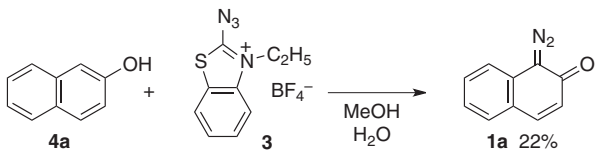



**Figure 1.** Diazonaphthoquinones.

naphthol undergoes the most efficient diazo-transfer reaction.[9] 1-Diazo-2(1*H*)-naphthalenone (**1a**) has been synthesized from 2-naphthol (**4a**) using the thiazolium salt **3**, although the yield was not high (22%) (eq 1).



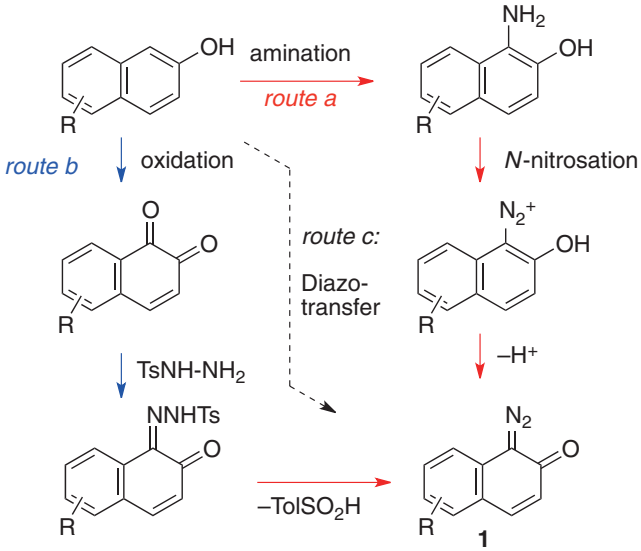

(1)

Recently, we have reported that 2-azido-1,3-dimethylimidazolinium salts **5** act as efficient reagents for diazo-transfer reactions with 1,3-dicarbonyl compounds (Table 1).[10] 2-Azido-1,3-dimethylimidazolinium chloride (ADMC, **5a**) has been prepared through the *N*-nitrosation of *N*-aminoguanidine **6** in an aqueous medium (Method A) or through the reaction between 2-chloro-1,3-dimethylimidazolinium chloride (DMC, **7**) and sodium azide in a nonaqueous solvent (Method B). The corresponding phosphate, 2-azido-1,3-dimethylimidazolinium phosphate (ADMP) **5b**, has been isolated as a crystal, and it has been found to be a stable and safe reagent.[11] ADMC **5a** and ADMP **5b** reacted with 1,3-dicarbonyl compounds under mild conditions in the presence of $Et_3N$ to give 2-diazo-1,3-dicarbonyl compounds in high yields. These 2-diazo-1,3-dicarbonyl compounds were easily isolated because the by-products of the reactions are highly soluble in water.

In a further study of the diazo-transfer reactions of the imidazolinium salts **5**,[12–14] we found that ADMC **5a** is able to transfer a diazo group to naphthols.[13] The outcomes of this reaction are described in this study.

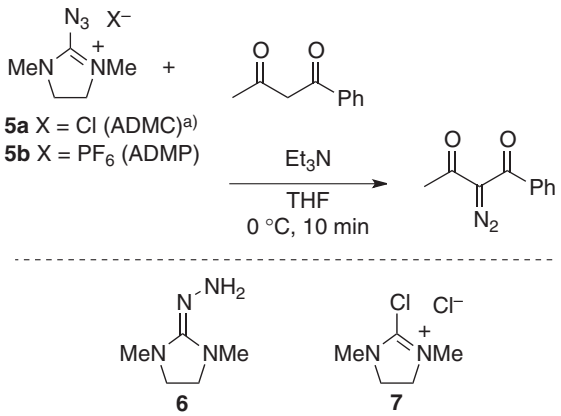
## Results and Discussion

We started with the reaction between ADMC **5a** (prepared using Method A) and 2-naphthol (**4a**) (Table 2). A solution of ADMC **5a** was prepared by stirring a mixture of guanidine **6**




**Scheme 1.** Synthesis of 1-diazonaphthoquinones **1**.

**Table 1.** Diazo-Transfer Reactions between 2-Azido-1,3-dimethylimidazolinium Salts **5** and 1,3-Dicarbonyl Compounds

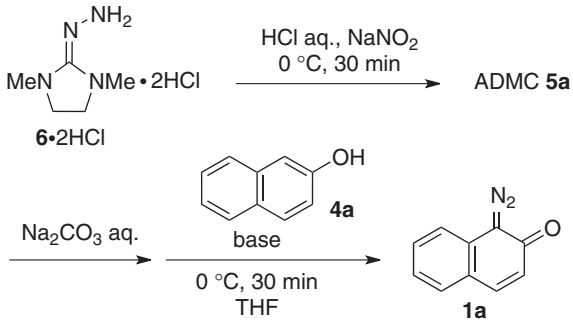



| Entry | X | **5** | Method[a)] | Yield/% |
|---|---|---|---|---|
| 1 | Cl | **5a** | A | quant. |
| 2 | Cl | **5a** | B | 98 |
| 3 | $PF_6$ | **5b** | — | 91 |

a) Methods for preparing ADMC **5a**. Method A: **6**·2HCl, HCl aq., $NaNO_2$, 0 °C, 30 min; $Na_2CO_3$ aq. Method B: DMC **7**, $NaN_3$, $CH_3CN$, 0 °C, 30 min.

and sodium nitrite in aqueous hydrochloric acid at 0 °C for 30 min. The pH of the mixture was adjusted to a value of 10 by adding saturated aqueous $Na_2CO_3$. Then, 2-naphthol (**4a**) was reacted with **5a** under different conditions. Adding 2-naphthol (**4a**) and $Et_3N$ at twice the molar concentration of **4a** in tetrahydrofuran (THF) led to the diazo-transfer product diazonaphthoquinone **1a** being obtained in 10% yield after stirring the mixture for 30 min (Entry 1). Adding sodium hydroxide rather than $Et_3N$ led to diazonaphthoquinone **1a** being obtained in 38% yield (Entry 2). Adding an excess of *N*-nitrosation reagents (HCl aq. and $NaNO_2$) increased the yield of diazonaphthoquinone **1a** to 52% (Entry 3). However, diazonaphthoquinone **1a** was found to decompose to naphthol **4a** in an aqueous

**Table 2.** Diazo-Transfer Reaction between ADMC **5a** and 2-Naphthol (**4a**) Using Method A[a)]




| Entry | HCl /equiv | $NaNO_2$ /equiv | Base | Yield/% | |
|---|---|---|---|---|---|
| | | | | **1a** | **4a** |
| 1 | 3 | 2.2 | $Et_3N$ | 10 | 88 |
| 2 | 3 | 2.2 | 1 M NaOH aq. | 38 | 56 |
| 3 | 5 | 5 | 1 M NaOH aq. | 52 | 44 |

a) Molar ratio: **6**·2HCl/**4a**/base = 1.1/1/2.

sodium hydroxide solution; therefore, we changed to performing the diazo-transfer reaction in an aprotic solvent in Method B.

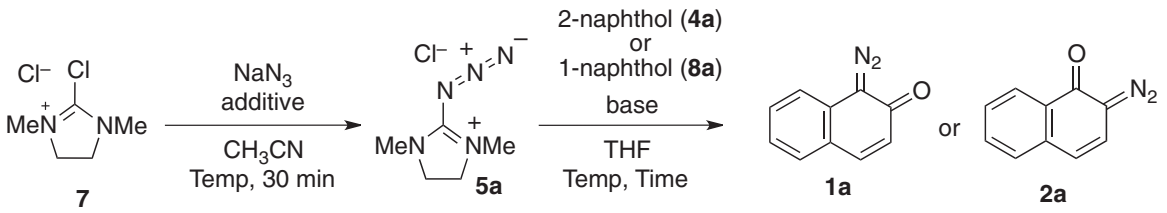
2-Naphthol (**4a**) was treated with 1.1 equiv of ADMC **5a** (prepared by the reaction between DMC **7** and sodium azide (Method B) in $CH_3CN$ at 0 °C) in THF in the presence of a base (Table 3, Entries 1–13). Using $Et_3N$ as a base led to diazonaphthoquinone **1a** being obtained in 58% yield (Entry 1). The effects of using different bases were remarkable. Using a base with a similar basicity to $Et_3N$, such as *i*-$Pr_2NEt_2$ or $K_2CO_3$, led to **1a** being obtained in a good yield (Entries 2 and 4), but using $Et_2NH$ led to **1a** being obtained in a poor yield (Entry 3). Less basic bases, such as aromatic bases, were not suitable for the production of diazonaphthoquinone **1a** (Entries 5–7). Using DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as a base led to **4a** being consumed and a large amount of an unknown product being observed when the product mixture was analyzed by thin layer chromatography (TLC) (Entry 8). However, these unknown products were not found, and **4a** was recovered in 66% yield, when the reaction was quenched by adding water.

The yield of **1a** increased to 80% when $Et_3N$ was used as the base and the reaction was performed at −20 °C, and the yield of **1a** increased to 86% when 1.5 equiv of ADMC **5a** was added (Entries 10 and 11). The reaction was accelerated when 30 mol % of 15-crown-5 was added (Entry 12). The reaction mixtures used in Entries 1–12 were not clear solutions, probably because of the poor solubility of sodium azide in the solvent mixture ($CH_3CN$ and THF) that was used. The reaction mixture was a clear solution when methanol was added, but this caused the yield of **1a** to decrease (Entry 13).

The reaction of 1-naphthol (**8a**) was then examined (Entries 14–17). 2-Diazo-1(2*H*)-naphthalenone (**2a**) was obtained regioselectively when 1-naphthol (**8a**) was used as a starting material, and adding 30 mol % of 15-crown-5 again effectively accelerated the reaction (Entries 14 and 15). However, adding too much of the crown ether was not effective in promoting the formation of diazonaphthoquinone **8a** (compare Entry 15 with Entries 16 and 17).

**Table 3.** Diazo-Transfer Reactions between ADMC **5a** and Naphthols **4a** and **8a** Using Method B




| Entry | Naphthol | Additive/equiv | Base | Temp/°C | Time | Product (Yield/%[a]) | |
|---|---|---|---|---|---|---|---|
| 1[b] | **4a** | — | $Et_3N$ | 0 | 1 h | **1a** (58) | **4a** (16) |
| 2[b] | **4a** | — | *i*-$Pr_2NEt$ | 0 | 1 h | **1a** (52) | **4a** (30) |
| 3[b] | **4a** | — | $Et_2NH$ | 0 | 1 h | **1a** (4) | **4a** (41) |
| 4[b] | **4a** | — | $K_2CO_3$ | 0 | 1 h | **1a** (53) | **4a** (21) |
| 5[b] | **4a** | — | DMAP | 0 | 1 h | **1a** (12) | **4a** (24) |
| 6[b] | **4a** | — | imidazole | 0 | 1 h | **1a** (5) | **4a** (59) |
| 7[b] | **4a** | — | pyridine | 0 | 1 h | **1a** (trace) | **4a** (77) |
| 8[b] | **4a** | — | DBU | 0 | 1 h | **1a** (0) | **4a** (66) |
| 9[b] | **4a** | — | — | 0 | 1 h | **1a** (0) | **4a** (84) |
| 10[b] | **4a** | — | $Et_3N$ | −20 | 1 h | **1a** (80) | |
| 11[c] | **4a** | — | $Et_3N$ | −20 | 1 h | **1a** (86) | |
| 12[c] | **4a** | 15-Crown-5 (0.3) | $Et_3N$ | −20 | 20 min | **1a** (87) | |
| 13[b] | **4a** | MeOH | $Et_3N$ | −20 | 1 h | **1a** (12) | **4a** (87) |
| 14[c] | **8a** | — | $Et_3N$ | −20 | 40 min | **2a** (76) | |
| 15[c] | **8a** | 15-Crown-5 (0.3) | $Et_3N$ | −20 | 30 min | **2a** (83) | |
| 16[c] | **8a** | 15-Crown-5 (1.3) | $Et_3N$ | −20 | 15 min | **2a** (72)[d] | |
| 17[c] | **8a** | 15-Crown-5 (2) | $Et_3N$ | −20 | 1 h | **2a** (41)[d] | |
| 18[e] | **4a** | | $Et_3N$ | 0 | 1 h | **1a** (27) | **4a** (43) |

a) Isolated yield. b) Molar ratio: **7**/$NaN_3$/naphthol **4a** or **8a**/$Et_3N$ = 1.1/1.2/1/2. c) Molar ratio: **7**/$NaN_3$/naphthol **4a** or **8a**/$Et_3N$ = 1.5/1.7/1/2. d) The yield was determined by $^1H$ NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. e) ADMP **5b** was used instead of ADMC **5a**. Molar ratio: ADMP **5b**/**4a**/$Et_3N$ = 1.1/1/2.

In contrast with the case of diazo-transfer reactions with 1,3-dicarbonyl compounds (Table 1, Entry 3), ADMP **5b** was unsuitable for a diazo-transfer reaction with naphthol under the optimized reaction conditions for ADMC **5a** (Table 3, Entry 18).

We investigated the diazotization of various naphthol derivatives to determine the scope and limitations of the method.

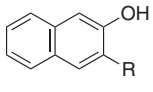
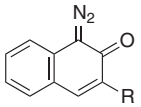
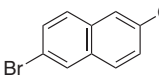
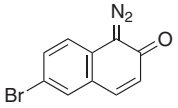
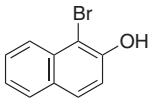
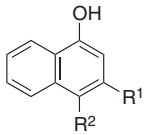
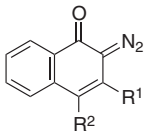
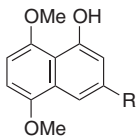
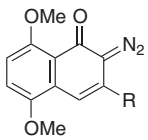
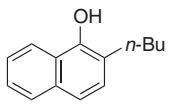
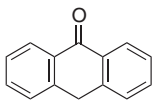
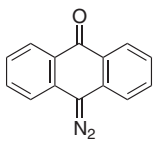
The results of performing the reaction using various naphthols (mono-ols) are shown in Table 4. 1-Unsubstituted 2-naphthols were converted into 1-diazonaphthoquinone in good yields (Entries 1–5), while 1-substituted 2-naphthols did not yield the corresponding diazo compounds (Entries 6 and 7). 2-Unsubstituted 1-naphthols gave 2-diazo derivatives in good yields, and the presence of substituents at the C(3) or C(4) positions on the 1-naphthol did not influence the yield (Entries 8–11). 5,8-Dimethoxy-1-naphthols were also transformed into the corresponding diazonaphthoquinones in good yields (Entries 12 and 13). The reaction became complex when the 1-naphthol had a substituent at the C(2) position, and we were not able to identify the compounds that were obtained (Entry 14).

Anthrone (equivalent to anthracene-9-ol) gave the corresponding diazo compound **9** in good yield (Entry 15), but phenol could not be used in the diazotization reaction (Entry 16).

Interestingly, 1-formyl-2-naphthol (**12**) reacted with ADMC **5a** at −20 °C to give isooxazole **13** in 70% yield accompanied by 1-diazonaphthoquinone **1a**, but reacting 1-formyl-2-naphthol (**12**) with ADMC **5a** at room temperature for a prolonged period led to the formation of 1-cyano-2-naphthol (**14**) in 70% yield (Scheme 2). The nitrile **14** would have been formed via **13** because **13** was confirmed to transform to **14** by the reaction with $Et_3N$ in THF at room temperature for 3 h.

The reaction with naphthalenediols was then examined (Table 5). The formation of monodiazotized compounds was not detected when 1,3-naphthalenediol (**15a**) was treated with 1.5 equiv of ADMC **5a**, but the bis-diazotized compound **16** was obtained in 61% yield. The yield of the bis-diazotized compound **16** increased to 80% when 3.0 equiv of **5a** was used (Entry 1). 1,5-Naphthalenediol (**15b**) was consumed by treating it with the azide imidazolinium **5a**, but the products were difficult to isolate. 5-Acetoxy-2-diazo-1(2*H*)-naphthalenone (**17**) was obtained in 56% yield when 1,5-naphthalenediol was diazotized using ADMC **5a** and the subsequent acetylation (using $Ac_2O$, in pyridine) of the product (Entry 2). Acetylation was performed after the diazo-transfer reaction with ADMC **5a** in all of the subsequent reactions with naphthalenediols so that the products could easily be isolated. The bis-diazotized compound was not obtained after the reaction of **15b** even though an excess of the diazotizing reagent **5a** was used. A monodiazotized compound was obtained regioselectively when 1,6-naphthalenediol (**15c**) was reacted (Entry 3). The diazo-transfer reaction of 1,7-naphthalenediol (**15d**) gave several

**Table 4.** Reactions of Naphthols with ADMC **5a**[a)]

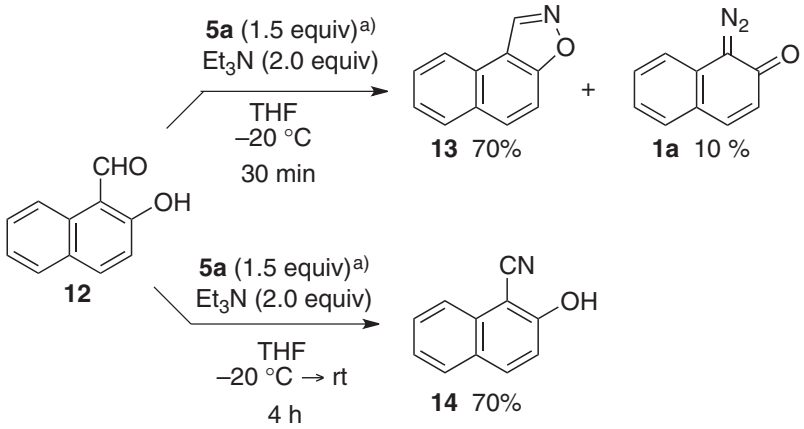
| Entry | ArOH | Time | Product | Yield/%[b)] |
|---|---|---|---|---|
| |  | |  | |
| 1 | **4b** (R = $CH_2OTBS$) | 0.5 h | **1b** (R = $CH_2OTBS$) | 81 |
| 2 | **4c** (R = $CO_2CH_3$) | 1 h | **1c** (R = $CO_2CH_3$) | 75 |
| 3 | **4d** (R = $CO_2Ph$) | 1 h | **1d** (R = $CO_2Ph$) | 62 |
| 4 | **4e** (R = CONHPh) | 1 h | **1e** (R = CONHPh) | 60 [93][c)] |
| 5 |  **4f** | 1 h |  **1f** | 79 |
| 6 |  **4g** | 3 h | —[d)] | |
| 7 | BINOL (**4h**) | 2 h | —[e)] | |
| |  | |  | |
| 8 | **8b** ($R^1$ = H, $R^2$ = OMe) | 1 h | **2b** ($R^1$ = H, $R^2$ = OMe) | 73 |
| 9 | **8c** ($R^1$ = H, $R^2$ = Cl) | 1 h | **2c** ($R^1$ = H, $R^2$ = Cl) | 81 |
| 10 | **8d** ($R^1$ = $CH_2OTBS$, $R^2$ = H) | 1 h | **2d** ($R^1$ = $CH_2OTBS$, $R^2$ = H) | 72 |
| 11 | **8e** ($R^1$ = $CO_2CH_3$, $R^2$ = H) | 2 h | **2e** ($R^1$ = $CO_2CH_3$, $R^2$ = H) | 98 |
| |  | |  | |
| 12[f)] | **8f** (R = (*E*)-CH=CH-Ph) | 3 h | **2f** (R = (*E*)-CH=CH-Ph) | 89 |
| 13 | **8g** (R = $CO_2C_2H_5$) | 4 h | **2g** (R = $CO_2C_2H_5$) | 60 |
| 14 |  **8h** | 1 h | —[d)] | |
| 15 |  **9** | 10 min |  **10** | [86][c),g)] |
| 16 |  **11** | 2 h[h)] | —[e)] | |

a) Unless otherwise noted, the reactions were carried out at −20 °C by stirring a mixture of ArOH (1 equiv) and $Et_3N$ (2 equiv) in THF with a solution of ADMC **5a** (1.5 equiv), which was prepared using DMC **7** (1.5 equiv), sodium azide ($NaN_3$) (1.7 equiv), and 15-crown-5 (30 mol %) in $CH_3CN$. b) Isolated yield. c) The yield was determined by $^1$H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. d) Complex mixture. No compounds were identified. e) Ar-OH was recovered. f) Molar ratio: **7**/$NaN_3$/**8f**/$Et_3N$ = 5/5/1/5. g) Anthraquinone was obtained in 7% yield. h) At room temperature.

products, and **19** and **20** were obtained as a 2:1 mixture in 60% yield and **19** was isolated in 12% yield (Entry 4). The 2,6-naphthalenediol **15e** and the 2,7-naphthalenediol **15f** gave the monodiazotized compounds **21** and **22**, respectively (Entries 5 and 6).

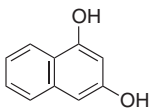
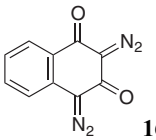
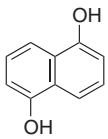
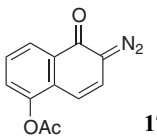
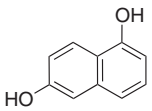
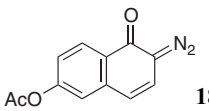
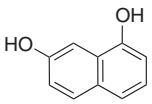
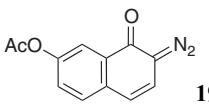
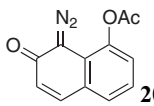
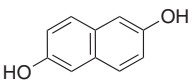
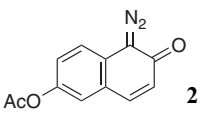
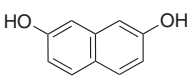
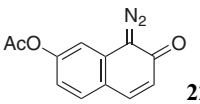
The optimized equilibrium geometry of 2-azido-1,3-dimethylimidazolinium **23** is shown in Figure 2 (B3LYP/6-31G**). There is no imaginary frequency in the calculated spectrum. Both the LUMO (solid) and the electron density surfaces (transparent) are shown in Figure 2b. The LUMO protrudes




**Scheme 2.** Reaction between 1-formyl-2-naphthol (**12**) and ADMC **5a**.

**Table 5.** Reactions of Naphthalenediols **15** with ADMC **5a**[a)]

| Entry | Naphthalenediol | **15** | Time | Product (Yield/%)[b)] |
|---|---|---|---|---|
| 1 |  | **15a** | 10 min |  **16** (80)[c)] |
| 2[d)] |  | **15b** | 1 h |  **17** (56) |
| 3[d)] |  | **15c** | 1 h |  **18** (41) |
| 4[d)] |  | **15d** | 30 min |  **19** (12 [40][e)])  **20** ([20][e)]) |
| 5[d)] |  | **15e** | 1 h |  **21** (31) |
| 6[d)] |  | **15f** | 30 min |  **22** (40) |

a) Unless otherwise noted, the reactions were carried out at −20 °C by stirring a mixture of ArOH and $Et_3N$ (2 equiv) in THF with a solution of ADMC **5a** (1.5 equiv), which was prepared from DMC **7** (1.5 equiv), sodium azide (1.7 equiv), and 15-crown-5 (30 mol %) in $CH_3CN$. b) Isolated yield. c) 3.0 equiv of **5a** was used. d) After the diazotization reaction was performed, the crude products were treated with acetic anhydride and pyridine. e) The yield was determined by $^1H$ NMR spectroscopy.

from the electron density surface around the terminal nitrogen. This figure suggests that a soft nucleophile would preferentially attack the terminal nitrogen of **5a** electrostatically.[15] A natural population analysis of **23** calculated at the same level of theory is shown in Table 6 (B3LYP/6-31G**). Large positive charge is localized at C(1) in **23**, which suggests that a hard nucleophile would attack C(1), preferably through a charge-controlled reaction.[15]

A plausible mechanism for the reaction between ADMC **5a** and 2-naphthol **4a** in the presence of a base is shown in Scheme 3. The reaction pathway depends on the base used. Naphtholate **I** will be formed from naphthol **4a** and the base at

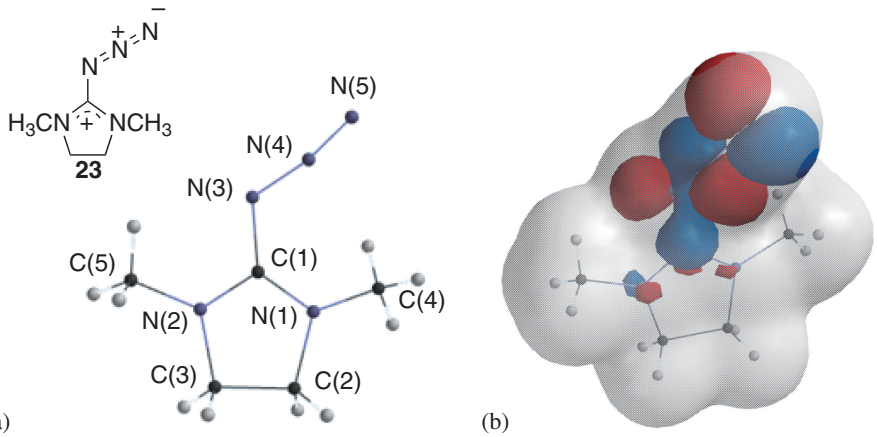
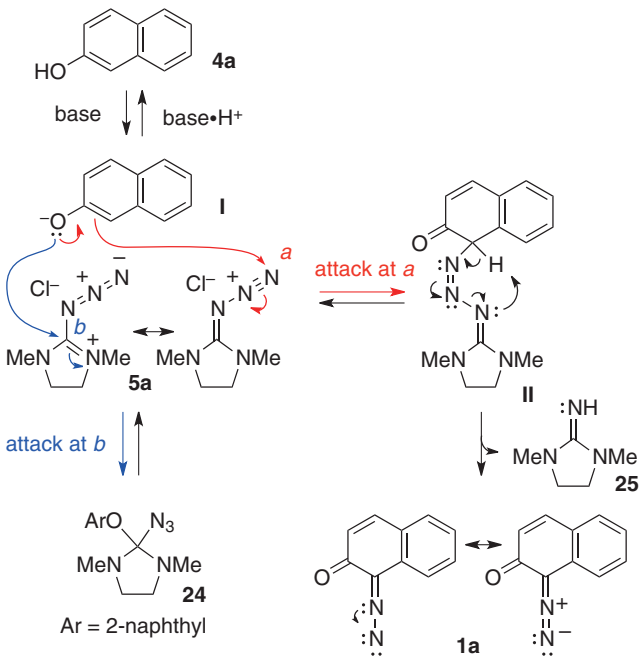



**Figure 2.** Optimized equilibrium geometry (B3LYP/6-31G**) of 2-azido-1,3-dimethylimidazolinium (ADM) **23** obtained using Spartan 08. (a) Optimized equilibrium geometry with numbers. (b) The LUMO (solid) and the electron density surface (transparent).

**Table 6.** Natural Population Analysis (B3LYP/6-31G**) for 2-Azido-1,3-dimethylimidazolinium (ADM) **23**

| Atom | Natural charge[a)] |
|---|---|
| N(1) | −0.421426 |
| N(2) | −0.390391 |
| N(3) | −0.344347 |
| N(4) | 0.223098 |
| N(5) | 0.133719 |
| C(1) | 0.672485 |
| C(2) | −0.268080 |
| C(3) | −0.271542 |
| C(4) | −0.499865 |
| C(5) | −0.491281 |

a) Sum of atomic charges = 1.000000.




**Scheme 3.** Plausible reaction mechanism.

equilibrium when the base used has a conjugate acid with an acidity similar to that of naphthol ($pK_a \approx 10$). Naphtholate **I** will then attack the terminal nitrogen in **5a** (the position *a* in **5a**) to form intermediate **II**. Intermediate **II** will then undergo intramolecular proton abstraction to afford the corresponding diazo compound **1a** and guanidine **25**. The reverse reaction will occur when naphtholate **I** attacks the central carbon in the guanidinium (the position *b* in **5a**), and naphtholate **I** and naphthol **4a** will be reformed at equilibrium. In contrast, naphtholate **I** will be kinetically formed when a strong base ($pK_{aH} > 10$) is used, and a hard oxygen nucleophile will attack the most positive position *b* in **5a** to form **24**. In this case, the reverse reaction will be slow because naphtholate **I** is predominantly formed from naphthol **2a**. Naphtholate **I** will hardly be formed when a weak base is used; therefore diazonaphthoquinone **1a** will not be formed efficiently.

X-ray structural data for diazoquinone have been reported in several publications,[16] but there are few reports of structural data for diazonaphthoquinones.[7g,17] We succeeded in determining X-ray structural data for the simple diazonaphthoquinones **1a**[18] and **2a**[19] (Figures 3 and 4). The $CN_2$ moiety is almost linear, with C–N(1)–N(2) bond angles of 175.50(14) and 176.92(11)° for **1a** and **2a**, respectively (Table 7). The N(1)–N(2) and C–N(1) bond lengths are 1.1210(19) and 1.3355(19) Å, respectively, for **1a**, and 1.1168(14) and 1.3482(14) Å, respectively, for **2a**. The N(1)–N(2) bond lengths are longer and the C–N(1) bond lengths are shorter than those in a benzenediazonium salt (the N(1)–N(2) and C–N(1) bond lengths in benzenediazonium tetrafluoroborate are 1.083 and 1.415 Å, respectively).[20] The ketone C=O bond lengths are 1.2474(19) Å in **1a** and 1.2409(13) Å in **2a**, and these lengths are close to the length of a double bond. The C=O bond lengths in benzoquinone are around 1.2 Å (1.195 Å for chloranil),[21] while the aromatic C–O bond lengths are around 1.37–1.40 Å (1.373(8) Å for 3,5-dichlorophenol).[22] Allen examined the relationships between N–N bond lengths and N–C bond lengths in diazo and diazonium compounds (compounds with a C–N≡N substructure).[16d] The average N–N and N–C bond lengths in α-diazoketones were found to be 1.115(3) and 1.328(5) Å,

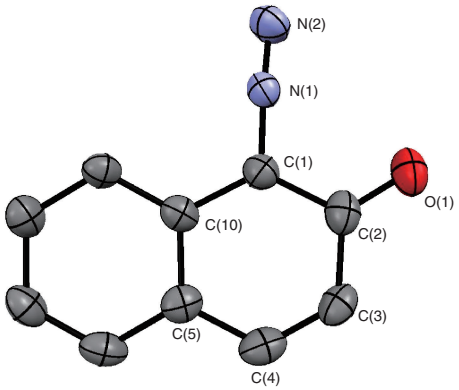



**Figure 3.** ORTEP of diazonaphthoquinone **1a**. The thermal ellipsoids are set at 50%. Hydrogen atoms are omitted for clarity.

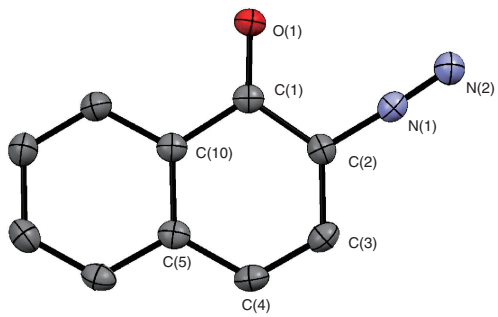



**Figure 4.** ORTEP of diazonaphthoquinone **2a**. The thermal ellipsoids are set at 50%. Hydrogen atoms are omitted for clarity.

respectively, and the N–N and N–C bond lengths in benzoylphenyldiazomethane were found to be 1.132(5) and 1.325(5) Å, respectively.[23] These data suggest that the diazonaphthoquinones **1a** and **2a** do not have diazoniumnaphtholate structures but have structures of diazo carbonyl compounds in the solid state.

## Conclusion

In conclusion, we have developed a general method for synthesizing diazonaphthoquinones by treating naphthol derivatives with 2-azido-1,3-dimethylimidazolinium chloride **5a**. The ease with which **5a** is prepared and the common use of naphthol imply that this method is likely to find widespread use in organic synthesis and material chemistry, such as for preparing photoresists.

## Experimental

**General.** All reactions were carried out under a nitrogen atmosphere unless otherwise noted. $^{1}$H NMR (400.1 MHz, 500.0 MHz) and $^{13}$C NMR (100.6 MHz, 125.7 MHz) spectra were recorded on a Bruker Avance 400 or JEOL JNM-A500 in $CDCl_3$ or DMSO-$d_6$ solutions [In $CDCl_3$, $CHCl_3$ (for 1H, $\delta = 7.26$) or $CDCl_3$ (for 13C, $\delta = 77.0$) was used as an internal standard. In DMSO-$d_6$, DMSO-$d_6$ (for $^{13}$C, $\delta = 39.95$) was used as an internal standard.]. IR spectra were recorded on a JEOL JIR-WINSPEC50. High-resolution mass spectra were obtained with a JEOL JMS-SX102A mass spectrometer. The melting points are uncorrected. Elemental analyses were recorded on a Yanaco MT-5, and carried out at Center for Instrumental Analysis, Faculty of Engineering, Kyusyu Institute of Technology. Column chromatography was performed on silica gel (Kanto silica gel 60N or Fuji Silysia Silica gel PSQ-100B). 2-Chloro-1.3-dimethyl-2-imidazolinium chloride was purchased from TCI or prepared following a literature procedure.[24]

**Table 7.** Selected Geometric Parameters for **1a** and **2a**; Distances in Å, Angle in °

| | **1a** | **2a**[a)] | |
|---|---|---|---|
| O(1)–C | 1.2474(19)[b)] | 1.2409(13)[c)] | [1.240(4)] |
| N(1)–N(2) | 1.1210(19) | 1.1168(14) | [1.106(5)] |
| N(1)–C | 1.3355(19)[d)] | 1.3482(14)[e)] | [1.339(5)] |
| C(1)–C(2) | 1.449(2) | 1.4468(15) | [1.451(5)] |
| C(2)–C(3) | 1.458(2) | 1.4307(16) | [1.413(5)] |
| C(3)–C(4) | 1.359(2) | 1.3495(17) | [1.342(5)] |
| C(4)–C(5) | 1.444(2) | 1.4431(16) | [1.438(5)] |
| C(5)–C(10) | 1.418(2) | 1.4195(15) | [1.400(5)] |
| C(10)–C(1) | 1.448(2) | 1.4779(14) | [1.460(5)] |
| N(2)–N(1)–C | 175.50(14)[f)] | 176.92(11)[g)] | [176.2(4)] |
| C(2)–C(1)–C(10) | 126.40(13) | 112.93(9) | [112.7(3)] |
| C(1)–C(2)–C(3) | 113.42(13) | 125.66(9) | [124.7(3)] |
| C(4)–C(5)–C(10) | 119.17(13) | 120.76(9) | [121.0(3)] |
| C(6)–C(5)–C(10) | 118.48(13) | 117.95(10) | [117.9(3)] |
| C(1)–C(10)–C(5) | 115.66(12) | 121.04(9) | [121.8(3)] |

a) The values in square brackets are quoted from Ref. 17. b) Distance of O(1)–C(2). c) Distance of O(1)–C(1). d) Distance of N(1)–C(1). e) Distance of N(1)–C(2). f) Angle of N(2)–N(1)–C(1). g) Angle of N(2)–N(1)–C(2).

*Caution: Although we have never had any trouble with azidoimidazolinium salts **5**, azide compounds are potentially explosive.*[25] *Reaction with **5** should be carried out in a well-ventilated hood, and should be conducted behind a safety shield.*

**Density Functional Calculations.** Computational studies were carried out using DFT calculations on Spartan 08 platform. Optimized equilibrium geometry was found by B3LYP functional and 6-31G** basis set. A natural population analysis was calculated at the same level of theory (B3LYP/6-31G**).

**Typical Procedure for the Preparation of Diazonaphthoquinones by the Reaction of 2-Naphthol (4a) with 2-Azide-1,3-dimethylimidazolinium Chloride (Method A, Table 2, Run 3):** To a solution of 1,3-dimethylimidazolidinonehydrazone dihydrochloride (**6**·2HCl) (228 mg, 1.1 mmol) in water (2.7 mL) was added conc. hydrochloric acid (0.45 mL, 5.4 mmol). To the mixture, sodium nitrite (346 mg, 5.0 mmol) in water was added slowly at 0 °C, and the mixture was stirred for 20 min. After the mixture was added aqueous sodium carbonate solution until pH ca. 10, an aqueous solution of 2-naphthol (**4a**, 162 mg, 1.0 mmol) and 1 M NaOH aq. (1.0 mL, 2.0 mmol) was added to the mixture, which was stirred for 30 min. From the mixture, organic materials were extracted three times with $CH_2Cl_2$. The combined extracts were washed with brine, and dried over anhydrous sodium sulfate. The solvent was removed in vacuo to afford crude compounds, which were purified by

flash column chromatography (silica gel: hexane/ethyl acetate) to give diazonaphthoquinone **1a** in 52% yield.

**Typical Procedure for the Preparation of Diazonaphthoquinones by the Reaction of Naphthols with 2-Azide-1,3-dimethylimidazolinium Chloride (Method B, Table 3, Run 12):** To a solution of 2-chloro-1,3-dimethylimidazolinium chloride **7** (228 mg, 1.35 mmol) in acetonitrile (2 mL), sodium azide (99.4 mg, 1.5 mmol) and 15-crown-5 ether (0.06 ml, 0.3 mmol) was added at −20 °C and the mixture was stirred for 30 min. 2-Naphthol **14a** (130 mg, 0.90 mmol) and triethylamine (0.25 mL, 1.8 mmol) in THF (4 mL) was added to the mixture, which was stirred for 20 min. The reaction was quenched with water, and organic materials were extracted three times with $CH_2Cl_2$. The combined extracts were washed with water and brine, and then, dried over anhydrous sodium sulfate. The solvent was removed in vacuo to afford crude compounds. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 4/1) to give diazonaphthoquinone **1a** in 87% yield.

**1-Diazo-2(1*H*)-naphthalenone (1a):** IR (ATR): 2333, 2221, 2084, 1616, 1558, 1479, 1452, 1394, 1346, 1304, 1251, 1203, 819, 613 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.62 (d, 1H, $J$ = 9.8 Hz), 7.57 (dd, 1H, $J$ = 7.8, 1.2 Hz), 7.51 (ddd, 1H, $J$ = 7.8, 7.8, 1.2 Hz), 7.28 (brd, 1H, $J$ = 7.8 Hz), 7.27 (ddd, 1H, $J$ = 7.8, 7.8, 1.2 Hz), 6.65 (d, 1H, $J$ = 9.8 Hz); $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 180.2, 140.2, 130.0, 129.7, 127.1, 125.9, 125.6, 124.7, 119.6, 77.2; Anal. Found: C, 70.76; H, 3.70; N, 16.39%. Calcd for $C_{10}H_6N_2O$: C, 70.58; H, 3.55; N, 16.46%.

**3-(*tert*-Butyldimethylsiloxymethyl)-1-diazo-2(1*H*)-naphthalenone (1b):** IR (KBr): 3446, 3055, 2954, 2856, 2099, 1587, 1119 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.73 (t, 1H, $J$ = 1.6 Hz), 7.61 (d, 1H, $J$ = 7.3 Hz), 7.45 (ddd, 1H, $J$ = 8.5, 7.5, 1.0 Hz), 7.28–7.24 (m, 2H), 4.40 (d, 2H, $J$ = 1.7 Hz), 0.99 (s, 9H), 0.15 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 179.1, 136.7, 134.5, 129.8, 128.8, 126.2, 125.6, 124.6, 119.3, 76.6, 60.3, 26.0, 18.4, −5.4 ppm; HRMS (FAB$^+$): $m/z$ $[M + H]^+$ Calcd for $C_{17}H_{23}N_2O_2Si$ 315.1529, found 315.1539.

**Methyl 4-Diazo-3,4-dihydro-3-oxo-2-naphthalenecarboxylate (1c):** IR (ATR): 2117, 1725, 1706, 1614, 1552, 1481, 1454, 1430, 1207, 1143, 1089 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.39 (s, 1H), 7.69 (d, 1H, $J$ = 7.8 Hz), 7.61 (ddd, 1H, $J$ = 7.8, 7.8, 1.1 Hz), 7.31 (dd, 1H, $J$ = 7.8, 7.8 Hz), 7.29 (d, 1H, $J$ = 7.8 Hz), 3.94 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 175.7, 165.3, 145.3, 131.9, 131.7, 129.2, 126.0, 125.0, 123.7, 119.3, 80.0, 52.5; Anal. Found: C, 63.23; H, 3.62; N, 12.34%. Calcd for $C_{12}H_8N_2O_3$: C, 63.16, H, 3.53; N, 12.28%; mp 92.5–94 °C (dec).

**Phenyl 4-Diazo-3,4-dihydro-3-oxo-2-naphthalenecarboxylate (1d):** IR (KBr): 3446, 2089, 1729, 1625, 1209 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.57 (s, 1H), 7.76 (d, 1H, $J$ = 7.7 Hz), 7.65 (ddd, 1H, $J$ = 8.0, 7.4, 1.1 Hz), 7.43 (dd, 2H, $J$ = 8.3, 7.4 Hz), 7.35 (dd, 2H, $J$ = 8.5, 7.7 Hz), 7.29–7.25 (m, 3H); $^{13}C$ NMR (101 MHz, DMSO-$d_6$): $\delta$ 174.8, 163.1, 150.9, 145.6, 132.6, 132.3, 130.0, 129.8, 126.4, 125.34, 125.29, 123.4, 122.3, 121.2, 80.8 ppm; HRMS (EI$^+$): $m/z$ $[M]^+$ Calcd for $C_{17}H_{10}N_2O_3$ 290.0691, found 290.0688.

**4-Diazo-3,4-dihydro-3-oxo-*N*-phenyl-2-naphthalenecarboxamide (1e):**[9] IR (ATR): 3026, 2844, 2690, 2476, 2360, 2283, 2106, 1676, 1595, 1589, 1358, 1209, 790.7 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 11.7 (s, 1H), 8.9 (s, 1H), 7.8 (d, 1H, $J$ = 7.8 Hz), 7.75 (d, 2H, $J$ = 8.0 Hz), 7.62 (ddd, 1H, $J$ = 7.8, 7.4, 1.1 Hz), 7.37–7.28 (m, 3H), 7.31 (d, 1H, $J$ = 7.8 Hz), 7.12 (t, 1H, $J$ = 7.8 Hz); $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 179.5, 161.3, 145.7, 138.3, 132.3, 132.0, 129.0, 128.7, 125.5, 125.2, 124.4, 124.3, 120.4, 119.1, 80.8; HRMS (FAB$^+$): Found: $m/z$ 290.0912. Calcd for $C_{17}H_{12}N_3O_2$: $(M + H)^+$, 290.0929; mp 152–153 °C (dec).

**6-Bromo-1-diazo-2(1*H*)-naphthalenone (1f):** IR (ATR): 2111, 1700, 1610, 1541, 1479, 1082, 820 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.71 (d, 1H, $J$ = 2.0 Hz), 7.60 (dd, 1H, $J$ = 8.5, 2.0 Hz), 7.54 (d, 1H, $J$ = 9.8 Hz), 7.15 (d, 1H, $J$ = 8.5 Hz), 6.69 (d, 1H, $J$ = 9.8 Hz); $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 179.5, 138.9, 132.5, 132.3, 127.1, 127.0, 125.9, 121.0, 117.8; Anal. Found: C, 48.23; H, 2.16; N, 11.04%. Calcd for $C_{10}H_5BrN_2O$: C, 48.22, H, 2.02; N, 11.25%; mp 105–115 °C (dec).

**2-Diazo-1(2*H*)-naphthalenone (2a):** IR (ATR): 2917, 2850, 2348, 2113, 1689, 1619, 1562 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.33 (d, 1H, $J$ = 8.0 Hz), 7.59 (ddd, 1H, $J$ = 8.0, 7.2, 1.4 Hz), 7.49 (d, 1H, $J$ = 7.2 Hz), 7.47 (ddd, 1H, $J$ = 8.0, 7.2, 1.4 Hz), 6.89 (d, 1H, $J$ = 9.3 Hz), 6.58 (d, 1H, $J$ = 9.3 Hz); $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 180.2, 137.47, 132.6, 129.5, 128.2, 127.2, 125.3, 117.3, 116.2, 74.2; Anal. Found: C, 70.20; H, 3.68; N, 16.74%. Calcd for $C_{10}H_6N_2O_3$: C, 70.58; H, 3.55; N, 16.46%; mp 73.5–74 °C (dec).

**4-Methoxy-2-diazo-1(2*H*)-naphthalenone (2b):** IR (ATR): 2364, 2337, 2136, 2025, 2084, 1733, 1623, 1610, 1556, 1471, 1448, 1332, 1155, 1128, 1095, 1035, 956 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.33 (dd, 1H, $J$ = 7.8, 1.1 Hz), 7.96 (d, 1H, $J$ = 7.9 Hz), 7.66 (ddd, 1H, $J$ = 7.9, 7.8, 1.3 Hz), 7.51 (ddd, 1H, $J$ = 7.9, 7.8, 1.1 Hz), 5.9 (s, 1H), 3.88 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 180.1, 144.4, 133.0, 132.6, 129.8, 127.9, 125.5, 122.5, 87.8, 74.6, 55.6; HRMS (FAB$^+$): Found: $m/z$ 201.0696. Calcd for $C_{11}H_9N_2O_2$: $(M + H)^+$, 201.0664; mp 104–105 °C (dec).

**4-Chloro-2-diazo-1(2*H*)-naphthalenone (2c):** IR (ATR): 2343, 2121, 1741, 1610, 1537 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.38 (dd, 1H, $J$ = 8.0, 1.0 Hz), 7.96 (dd, 1H, $J$ = 8.0, 1.0 Hz), 7.75 (ddd, 1H, $J$ = 8.0, 8.0, 1.0 Hz), 7.56 (ddd, 1H, $J$ = 8.0, 8.0, 1.0 Hz), 7.04 (s, 1H); $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 178.9, 134.9, 133.2, 130.2, 128.2, 125.9, 125.3, 118.0, 114.2, 79.89; HRMS (FAB$^+$): Found: $m/z$ 205.0176. Calcd for $C_{10}H_5ClN_2O_2$: $(M + H)^+$, 205.0169; mp 155–160 °C (dec).

**3-(*tert*-Butyldimethylsiloxymethyl)-2-diazo-1(2*H*)-naphthalenone (2d):** IR (KBr): 3446, 2929, 2858, 2117, 1624 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.30 (d, 1H, $J$ = 7.4 Hz), 7.60 (ddd, 1H, $J$ = 8.4, 7.0, 1.4 Hz), 7.46–7.42 (m, 2H), 6.44 (s, 1H), 4.70 (d, 2H, $J$ = 0.8 Hz), 0.92 (s, 9H), 0.11 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ 180.6, 136.6, 132.6, 129.8, 128.7, 127.9, 126.9, 125.3, 114.2, 77.7, 63.8, 25.7, 18.2, −5.5 ppm; HRMS (EI$^+$): $m/z$ $[M]^+$ Calcd for $C_{17}H_{22}N_2O_2Si$ 314.1451, found 314.1442.

**Methyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (2e):** IR (KBr): 3061, 2954, 2105, 1708, 1614, 1442, 1239 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.35 (dd, 1H, $J$ = 6.7, 0.7 Hz), 7.68 (ddd, 1H, $J$ = 8.1, 7.0, 1.4 Hz), 7.61 (d, 1H, $J$ = 6.2 Hz), 7.58 (ddd, 1H, $J$ = 7.9, 6.7, 1.2 Hz), 7.45 (s, 1H),

3.22 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 179.4, 164.0, 134.8, 133.0, 131.0, 130.0, 129.8, 125.8, 123.2, 119.1, 76.8, 53.0 ppm; HRMS (EI$^+$): $m/z$ $[M]^+$ Calcd for $C_{12}H_8N_2O_3$ 228.0535, found 228.0538.

**2-Diazo-5,8-dimethoxy-3-[(*E*)-2-phenylethenyl]-1(2*H*)-naphthalenone (2f):** IR (KBr): 2917, 2848, 2682, 2943, 2086, 1616, 1454, 1265, 1106 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.53 (d, 2H, $J = 7.0$ Hz), 7.41–7.28 (m, 5H), 7.02 (d, 1H, $J = 9.0$ Hz), 6.98 (d, 1H, $J = 16.0$ Hz), 6.85 (d, 1H, $J = 8.5$ Hz), 3.96 (s, 3H), 3.93 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ 174.4, 152.5, 149.1, 136.3, 132.5, 129.0, 128.8, 128.5, 126.8, 126.2, 122.8, 116.6, 113.1, 109.1, 89.2, 56.4, 56.2 ppm.

**3-Diazo-3,4-dihydro-5,8-dimethoxy-4-oxo-2-naphthalenecarboxylic Acid Methyl Ester (2g):** IR (ATR): 2918, 2848, 2241, 2104, 1709, 1614, 1578, 1462, 1373, 1255, 1105, 980; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.87 (s, 1H), 7.09 (d, 1H, $J =$ 9.0 Hz), 7.01 (d, 1H, $J = 9.0$ Hz), 3.95 (s, 6H), 3.93 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 163.9, 153.1, 150.1, 126.9, 120.5, 118.3, 117.0, 114.2, 112.8, 77.2, 56.7, 56.2, 52.7; HRMS (FAB$^+$): Found: $m/z$ 289.0835. Calcd for $C_{14}H_{13}N_2O_5$: $(M + H)^+$ 289.0824; mp 165.5–166 °C (dec).

**10-Diazo-9(10*H*)-anthracenone (10):**[9] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.52 (d, 2H, $J = 8.0$ Hz), 7.68 (ddd, 2H, $J = 7.1$, 7.2, 1.4 Hz), 7.39 (ddd, 2H, $J = 7.6$, 7.6, 1.0 Hz), 7.31 (d, 2H, $J = 8.0$ Hz); HRMS (FAB$^+$): Found: $m/z$ 221.0718 Calcd for $C_{14}H_9N_2O$: $(M + H)^+$, 221.0715.

**Naphth[1,2-d]isoxazole (13):**[26] IR (ATR): 3097, 3064, 2916, 2848, 1975, 1913, 1764, 1670, 1664, 629, 1581, 1560, 1531, 1512, 1485, 1466, 1446, 1431, 1392, 1342, 1331, 1288, 1265, 1253, 1221, 1207, 1167, 1138, 1088, 1001, 962; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.10 (d, 1H, $J = 1.0$ Hz), 8.14 (d, 1H, $J = 8.3$ Hz), 7.99 (brd, 1H, $J = 8.3$ Hz), 7.96 (d, 1H, $J = 9.1$ Hz), 7.73 (dd, 1H, $J = 9.1$, 0.9 Hz), 7.69 (ddd, 1H, $J = 9.1$, 7.1, 1.2 Hz), 7.57 (ddd, 1H, $J = 9.1$, 7.1, 1.2 Hz); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 162.2, 144.9, 131.7, 130.4, 129.0, 128.6, 126.7, 125.6, 123.2, 116.4, 110.2; Anal. Found: C, 77.94; H, 4.33; N, 8.14%. Calcd for $C_{11}H_7NO$: C, 78.09; H, 4.17; N, 8.28%; mp 77.5 °C.

**1-Cyano-2-naphthol (14):**[27] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.03 (d, 1H, $J = 8.3$ Hz), 7.95 (d, 1H, $J = 9.0$ Hz), 7.82 (d, 1H, $J = 8.1$ Hz), 7.65 (ddd, 1H, $J = 8.2$, 7.0, 1.2 Hz), 7.46 (ddd, 1H, $J = 8.1$, 7.1, 1.0 Hz), 7.18 (d, 1H, $J = 9.0$ Hz); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 162.2, 135.3, 132.9, 129.1, 128.6, 128.0, 125.2, 123.9, 117.4, 115.7, 92.7.

**2,4-Bis(diazo)-1,3(2*H*,4*H*)-naphthalenedione (16):**[4g] IR (ATR): 2919, 2597, 2348, 2088, 2026, 1687, 1591 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.24 (dd, 1H, $J = 8.0$, 1.2 Hz), 7.65 (ddd, 1H, $J = 8.0$, 8.0, 1.2 Hz), 7.33 (ddd, 1H, $J = 8.0$, 8.0, 1.0 Hz), 7.15 (brd, 1H, $J = 8.0$ Hz); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 176.6, 173.6, 134.3, 127.7, 127.4, 125.6, 120.1, 120.1, 84.2; HRMS (FAB$^+$): Found: $m/z$ 213.0387. Calcd for $C_{10}H_4N_4O_2$: $(M + H)^+$, 213.0414; mp 180–183 °C.

**Typical Procedure for the Preparation of Diazonaphthoquinones Having Acetoxy Group by the Reaction of Naphthalenediols with 2-Azide-1,3-dimethylimidazolinium Chloride 5a and the Successive Acetylation (Table 5, Run 2).** To a solution of 2-chloro-1,3-dimethylimidazolinium chloride **7** (228 mg, 1.35 mmol) in acetonitrile (2 mL), sodium azide (99.4 mg, 1.5 mmol) and 15-crown-5 ether (0.06 ml, 0.3 mmol) was added at −20 °C and the mixture was stirred for 30 min. 1,5-Naphthalene diol **15b** (144 mg, 0.9 mmol) and triethylamine (0.25 mL, 1.8 mmol) in THF (4 mL) was added to the mixture, which was stirred for 1 h. To the mixture, acetic anhydride (0.17 mL, 1.8 mmol) and triethylamine (4.0 mL, 29 mmol) was added, and the mixture was stirred until diazonaphthoquinone was consumed by monitoring with TLC. The reaction was quenched with water, and organic materials were extracted three times with $CH_2Cl_2$. The combined extracts were washed with water and brine, and then, dried over anhydrous sodium sulfate. The solvent was removed in vacuo to afford crude compounds. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 4/1) to give **17** in 56% yield.

**5-Acethoxy-2-diazo-1(2*H*)-naphthalenone (17):** IR (ATR): 2924, 2412, 2200, 2098, 1749, 1608, 1581, 1450, 1408, 1373, 1321, 1265, 1211, 1165, 1024, 933 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.23 (ddd, 1H, $J = 7.9$, 1.3, 1.0 Hz), 7.46 (dd, 1H, $J = 7.9$, 7.9 Hz), 7.39 (dd, 1H, $J = 7.9$, 1.3 Hz), 6.93 (d, 1H, $J = 9.6$ Hz), 6.61 (dd, 1H, $J = 9.6$, 1.0 Hz), 2.41 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 179.2, 169.1, 146.6, 130.9, 130.3, 127.2, 126.0, 123.3, 117.2, 110.2, 77.8, 20.9; Anal. Found: C, 62.78; H, 3.58; N, 12.65%. Calcd for $C_{12}H_8N_2O_3$: C, 63.16; H, 3.53; N, 12.28%; mp 103–105 °C (dec).

**6-Acethoxy-2-diazo-1(2*H*)-naphthalenone (18):** IR (ATR): 3064, 2916, 2850, 2104, 1757, 1606, 1566, 1471, 1444, 1429, 1367, 1298, 1192, 1011, 957 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.34 (d, 1H, $J = 8.7$ Hz), 7.23 (d, 1H, $J =$ 2.2 Hz), 7.17 (dd, 1H, $J = 8.7$, 2.2 Hz), 6.91 (d, 1H, $J =$ 9.3 Hz), 6.50 (d, 1H, $J = 9.3$ Hz), 2.34 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 179.1, 168.9, 153.9, 138.9, 127.4, 126.5, 120.1, 117.5, 116.7, 77.5, 21.1; HRMS (FAB$^+$): Found: $m/z$ 229.0645. Calcd for $C_{12}H_9N_2O_3$: $(M + H)^+$, 229.0613; mp 107–115 °C.

**7-Acethoxy-2-diazo-1(2*H*)-naphthalenone (19):** IR (neat): 2109, 1761, 1624, 1580, 1213 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.01 (d, 1H, $J = 2.4$ Hz), 7.51 (d, 1H, $J =$ 8.5 Hz), 7.36 (dd, 1H, $J = 8.5$, 2.4 Hz), 6.87 (d, 1H, $J =$ 9.4 Hz), 6.57 (d, 1H, $J = 9.4$ Hz), 2.34 (s, 3H);$^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 179.1, 169.3, 149.4, 135.3, 130.4, 129.5, 126.5, 117.6, 116.4, 116.2, 77.1, 21.0; HRMS (FAB$^+$): Found: $m/z$ 229.0645. Calcd for $C_{12}H_9N_2O_3$: $(M + H)^+$, 229.0613.

**6-Acethoxy-1-diazo-2(1*H*)-naphthalenone (21):** IR (ATR): 3423, 2923, 2852, 2096, 1766, 1624, 1572, 1483, 1363, 1217, 1147, 1020, 906 cm$^{-1}$; $^1$H NMR: $\delta$ 7.59 (d, 1H, $J = 9.8$ Hz), 7.36–7.34 (m, 1H), 7.28–7.26 (m, 2H), 6.71 (d, 1H, $J = 9.8$ Hz), 2.34 (s, 3H); $^{13}$C NMR: $\delta$ 179.9, 169.4, 147.5, 139.4, 126.8, 126.2, 124.7, 123.7, 122.3, 120.6, 68.1, 21.0; HRMS (FAB$^+$): Found: $m/z$ 229.0640. Calcd for $C_{12}H_9N_2O_3$: $(M + H)^+$, 229.0613; mp 143–148 °C (dec).

**7-Acethoxy-1-diazo-2(1*H*)-naphthalenone (22):** IR (ATR): 2212, 2088, 1765, 1714, 1622, 1575, 1487, 1440, 1394, 1369, 1288, 1213, 1009, 918 cm$^{-1}$; $^1$H NMR: $\delta$ 7.59 (d, 1H, $J = 9.8$ Hz), 7.55 (d, 1H, $J = 8.4$ Hz), 7.01 (d, 1H, $J =$ 2.0 Hz), 6.98 (dd, 1H, $J = 8.4$, 2.0 Hz), 6.61 (d, 1H, $J =$ 9.8 Hz), 2.33 (s, 3H); $^{13}$C NMR: $\delta$ 179.7, 169.0, 151.8, 139.6, 131.2, 128.7, 125.6, 123.3, 118.7, 112.5, 77.5, 21.1; HRMS (FAB$^+$): Found: $m/z$ 229.0629. Calcd for $C_{12}H_9N_2O_3$: $(M + H)^+$, 229.0613; mp 103–105 °C (dec).

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## Supporting Information

Cartesian coordinates of computational data for 2-azido-1,3-dimethylimidazolinium **23**. This material is available electronically on J-STAGE.

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