An Unusual, DDQ-Promoted Oxidative Rearrangement of 9,9-Disubstituted 1,4,5,8-Tetrahydro-4a,8a-methanonaphthalenes

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The action of excess DDQ on 1,4,5,8-tetrahydro-4a,8a-methanonaphthalenes bearing a methyl group and one other substituent (cyclopropyl, methyl, phenyl) at the 9 position resulted in a peculiar oxidative rearrangement to 1-vinylnaphthalene derivatives. Two closely related mechanisms, both of which involve a 1,5-sigmatropic shift of the one-carbon bridge (Berson-Willcott rearrangement), are considered for this novel process.

More than four decades ago, Vogel announced that the bromination of both double bonds in **1**, followed by quadruple dehydrobromination in base, led to the aromatic hydrocarbon 1,6-methano[10]annulene (**2**).[1] A few years following this remarkable synthesis (Figure 1), Nelson and Untch demonstrated that the conversion of **1** into **2** can be accomplished quite expeditiously by direct oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[2]

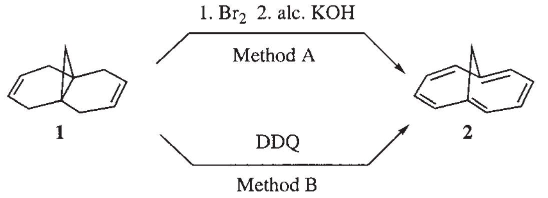
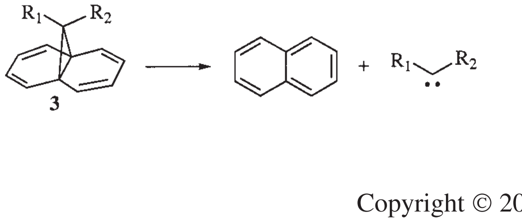


Figure 1. Vogel synthesis (method A) and Nelson and Untch synthesis (method B) of 1,6-methano[10]annulene.

In the course of our search for nonnitrogenous precursors to carbenes, we became interested in the 1,6-methano[10]annulene systems because of their known ability to extrude carbenes,[3] probably via the ring-closed form **3** (equation 1). Specifically, we sought to prepare a precursor to cyclopropylmethylcarbene (**3**, $R_1 = CH_3$ and R_2 = cyclopropyl) by oxidizing 9-cyclopropyl-9-methyl-1,4,5,8-tetrahydro-4a,8a-methanonaphthalene (**6a**, $R_1 = CH_3$ and R = cyclopropyl) with DDQ. The synthesis of **6a** was carried out as shown in Figure 2. Unexpectedly, however, the DDQ oxidation of **6a** led to 1-(1-cyclopropylvinyl)naphthalene (**7a**) in a yield of 75%.[4] Puzzled by this outcome, we synthesized **6b** and **6c** and discovered that these two compounds also rearranged to give the corresponding vinylnaphthalene derivatives **7b** and **7c** when subjected to DDQ oxidation (Figure 2), albeit in lower yields of 26% and 24% respectively. In all cases, the by-products included naphthalene and other partially oxidized substrates (*vide infra*).



(1)

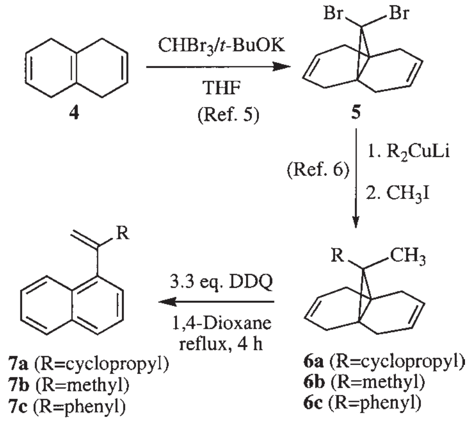


Figure 2. The synthesis of **6a-c** and their DDQ-promoted rearrangement to **7a-c**.

Rearrangements by way of alkyl and aryl shifts are not uncommon during DDQ oxidations.[7] To the best of our knowledge, however, the conversion of **6** into **7** appears to be a unique process that raises intriguing mechanistic questions. One possibility is that a Berson-Willcott rearrangement,[8] exemplified by the 1,5-sigmatropic carbon shift in equation 2, plays a key role in the mechanism.

(2)

Indeed, related shifts are known to occur in the methano[10]-annulene systems. For example, a single 1,5-carbon shift occurs in the parent hydrocarbon (**3**, $R_1 = R_2 = H$) upon flash vacuum pyrolysis at 500 °C,[9] and in its 11,11-dicyanoderivative at room temperature.[10] In the latter compound, two 1,5-shifts of carbon occur at 99 °C.[11] A similar "double shift" also accompanies the reaction of the monoester derivative (**3**, $R_1 = H$, $R_2 = CO_2CH_3$) under electrophilic acylation conditions.[12] Given these precedents, the two mechanistic routes from **6** to **7**, outlined in Figure 3, seem plausible.

Thus, in accord with what is known about DDQ dehydrogenations,[7] abstraction of a hydride ion from the allylic position in **6** followed by deprotonation gives a mixture of isomeric partially oxidized trienes **8**. A 1,5-carbon shift in **8** leads to **9** that can then lose a hydride ion to DDQ and open the cyclopropyl ring to give cation **10**. Orbital symmetry considerations suggest that if the 1,5-shift were concerted, the *exo* and *endo* dispositions of the two substituents on the migrating carbon (X and Y in equation 2) will change.[12] It is conceivable therefore that hydride abstraction from **9** by DDQ might be influenced by steric factors depending on whether the methyl group is *endo* or *exo*.

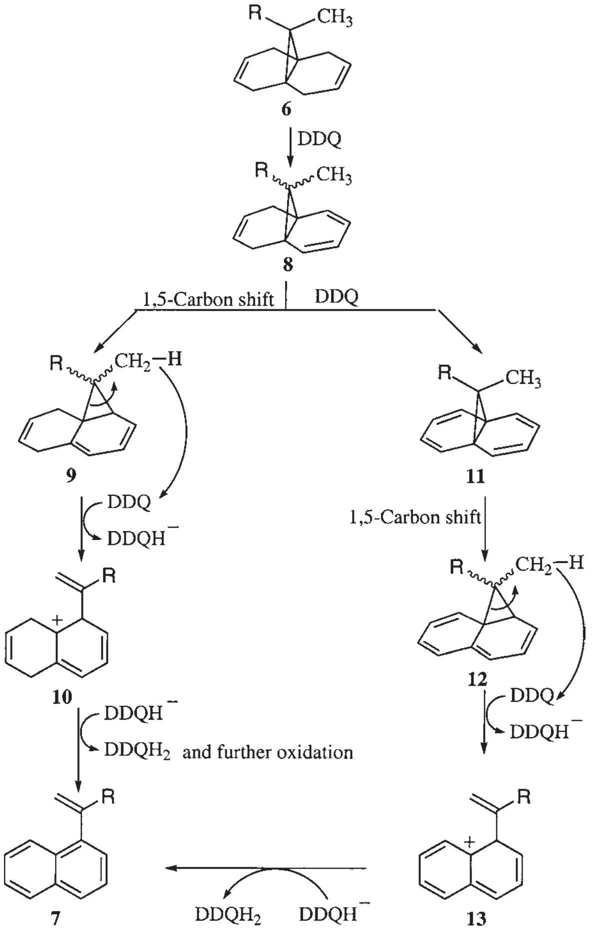


Figure 3. Two related mechanistic routes for the oxidative rearrangement **6** to **7**.

Finally, deprotonation of **10** followed by another DDQ dehydrogenation completes the sequence to afford the observed naphthalene derivative **7** (Figure 3).

Alternatively, further oxidation of **8** gives the methano[10]-annulene derivative **11** which undergoes a 1,5-carbon shift to produce **12**. The cation **13** could then issue from **12** by a process that is analogous to the conversion of **9** into **10**. In the last step, deprotonation of **13** leads to **7**.

We have also determined that the monomethyl substrate **14** gives the annulene derivative **15** without rearrangement to vinylnaphthalene (**16**) when subjected to DDQ oxidation (Figure 4). Thus it appears that two substituents are necessary at the 9 position to induce the oxidative rearrangement. It is yet to be determined, however, whether one of the two groups is required to be a methyl in order for the rearrangement to occur. Further investigations into the scope and mechanism of this interesting reaction are now underway in our laboratory as are computational studies to model key steps in the proposed mechanisms.

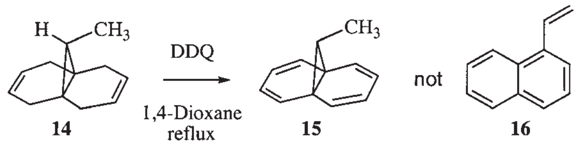


Figure 4. DDQ oxidation of **14** gives the annulene **15** instead the rearranged product **17**.

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