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Discovery and Mechanistic Study of a Totally Organic $C_{(aryl)}-C_{(alkyl)}$ Oxygen Insertion Reaction

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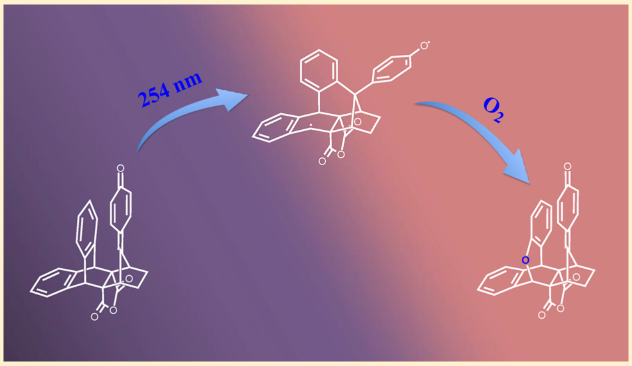
Supporting Information

ABSTRACT: We report an unprecedented photochemical oxygen insertion reaction into an aromatic quinone methide. Insertion happens specifically within a $C_{(aryl)}-C_{(alkyl)}$ bond, whereas the quinone methide moiety remains intact itself. Detailed mechanistic studies, supported by DFT calculations, support a pathway in which the *p*-QM plays a pivotal activating role.



The insertion of an oxygen atom into a C−C bond is often facile when one of the carbon atoms is part of an acyl group. The archetypical example, the eponymous Baeyer−Villager insertion reaction,[1] is synthetically highly useful[2] and its mechanistic details, highly reliant on nucleophilic attack on the carbonyl, are straightforward and well-understood.[3] One established pathway involves nucleophilic attack of peroxide at the electrophilic acyl carbon; thereupon, alkyl (or aryl) migration results in scission of the weak O−O bond and formation of the product (Figure 1).

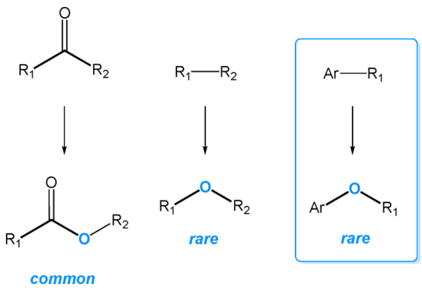


Figure 1. Oxygen insertion motifs.

On the other hand, insertion of an oxygen atom into other types of C−C bonds varies from extremely rare to all but nonexistent. Insertion of an oxygen atom from O_2 itself presents an even greater level of complexity as a stronger bond must be broken in the process. Selective insertion into a $C_{(aryl)}-C_{(alkyl)}$ bond is known in only a very few instances; the most notable example involves the work of Cristobal et al.[4] wherein an oxygen atom is inserted into an $C_{aromatic}-C_{sp^3}$ carbon of a transition-metal complex. In this system, the presence of a proximate N−H bond and an iridium center are necessary for the oxygen insertion to proceed. In any case, the mechanism by which this oxygenation occurs remains mysterious and its understanding out of reach, such that the authors themselves state: "it has to be noted that, as in the case of many O_2 mediated reactions with organic or organometallic substrates, it is not possible to advance mechanistic proposals for the oxidations described herein." The present system, as shall be seen, proves more amenable to mechanistic investigation.

Our studies began with recently reported *p*-quinone methide (*p*-QM) **1**,[5] which displays a variety of unusual reaction chemistry. We photolyzed *p*-QM **1** at various wavelengths with the rather vague goal of inducing a dimerization reaction, known to happen in other quinone methides.[6] Instead, we observed a highly selective oxygen insertion reaction at the *proximate* aromatic ring (Scheme 1). Evidently, the trace amounts of oxygen in the reaction mixture sufficed to ensure conversion. When the reaction is run under a pure oxygen atmosphere, both the rate and yield (90% conversion by NMR) of the reaction increase markedly. The ^1H NMR of the product reveals that the mirror plane bisecting the starting material has been annihilated. Unlike in *p*-QM **1**, the bridge protons appear at different chemical shifts, i.e., 3.45 and 3.88 ppm for the allylic protons and 4.16 and 5.5 ppm for the benzylic bridge protons. The precise structure of the product was confirmed by X-ray crystallography (Figure 2, also see the Supporting Information).

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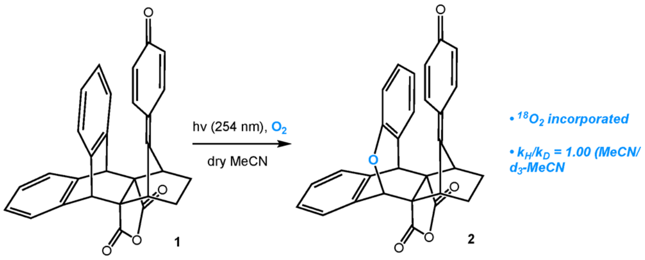
Scheme 1. Photooxygenation of p-QM 1



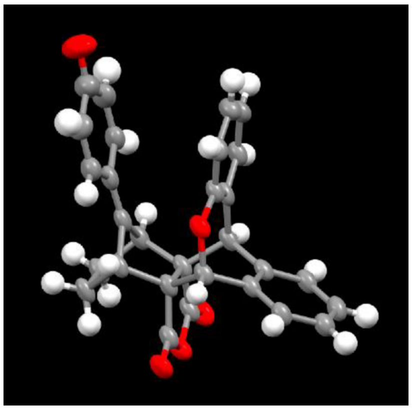
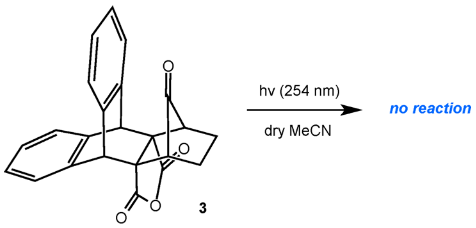


Figure 2. X-ray crystal structure of **2**.

■ MECHANISTIC STUDIES

The first and most important clue is stereochemical. As stated, the oxygenation reaction occurs exclusively across a C−C bond proximal to the QM moiety, suggesting its involvement in an important way. With this hint in mind, we undertook some simple control experiments to narrow the range of mechanistic possibilities. For example, ketone **3**[7] undergoes *no* oxygenation (no transformation whatsoever) under identical conditions, confirming that the QM moiety is necessary for oxygenation to occur. Moreover, ketone **3** also fails to oxygenate (at all wavelengths probed) in the presence of singlet oxygen sensitizers (e.g., rose bengal[8]) and strong excited-state electron acceptors such as 1,2,4,5-tetracyanobenzene.[9] In all cases, ketone **3** was quantitatively recovered (Scheme 2).

Scheme 2. Photooxygenation of Control 3



Conclusive evidence for the source of the incorporated oxygen atom comes from a simple labeling study employing $^{18}O{=}^{18}O$ gas, whereupon the ^{18}O label appears cleanly in the product. The role of the solvent provides additional clues; photolysis works comparably well in MeCN, PhCN, and *t*-BuCN, whereas photolysis in $PhCF_3$ and other aprotic solvents (also oxygenated) results in recovered starting material. The kinetic isotope effect (KIE) for photolysis in d_3-MeCN is approximately 1.0.

Several conclusions can be drawn from these results: (1) protic solvents are not necessary for successful oxygenation, suggesting that hydrogen atoms (or protons) are not transferred at any point in the process; (2) the lack of a hydrogen-based KIE is also congruent with this fact; (3) non-nitrilic, nonprotic solvents, in contrast, produce *no oxygen insertion product*; (4) nitrile-based solvents are apparently necessary for success, suggesting a *chemical role* for them in the mechanism; and (5) in the presence of water, oxygenation is overridden in favor of hydrolysis, a fact that will be discussed below.

With these data in hand, a plausible mechanistic scenario takes shape that is supported by both experiments and calculations (Scheme 3; see the Supporting Information for computational details). Excitation (254 nm) produces an aromatic ring centered excited state ($\mathbf{1}_{\mathbf{S1}}$*) that engages in intramolecular cyclization with the proximate QM moiety[10] through transition state $\mathbf{TS1}_{\mathbf{S1}}$ located 65.1 kcal mol^{-1} above the starting substrate $\mathbf{1}_{\mathbf{S1}}$ (calculations performed at the IEFPCM[MeCN] M06-2X/6-311+G(2d,2p)//B3LYP/6-31G(d) level using the program Gaussian 09). The key features of this transition state, C−C bond breaking and bond forming distances of 2.21 Å and 1.66 Å, respectively, lead to relatively stable benzyl diradical $\mathbf{4}_{\mathbf{S1}}$ with a lifetime sufficient to trap molecular oxygen (still a fast process). The reaction of O_2 with free radicals is known to be rapid,[11] and, in this case, forms triplet peroxyradical $\mathbf{5}_{\mathbf{T1}}$ from transient $\mathbf{4}_{\mathbf{S1}}$, which is electrophilic at the peroxyl group and relatively more nucleophilic at the phenol oxygen (calculated NBO charges of −0.18 and −0.58 eV, respectively). Reaction with the abundant solvent (namely a nitrile of some sort) then occurs to afford intermediate $\mathbf{6}_{\mathbf{T1}}$. With the stage set—with the orbital alignment excellent and electronic polarization optimal—facile scission of the O−O bond (distance = 1.60 Å) by $\mathbf{TS2}_{\mathbf{T1}}$ with a computed Gibbs free activation energy ($\Delta G^{\ddagger}$) of only 0.1 kcal mol^{-1} releases a transient, putative nitrile oxide[12] byproduct and diradical $\mathbf{7}_{\mathbf{T1}}$. This diradical species, stereoelectronically well positioned for pseudoaxial oxygen attack upon the neighboring aromatic ring, then reacts to form resonance-stabilized aryl radical $\mathbf{8}_{\mathbf{T1}}$ by C−O bond forming (distance = 1.92 Å) transition state $\mathbf{TS3}_{\mathbf{T1}}$ with an activation barrier of 10.4 kcal mol^{-1}. Subsequent C−C bond homolysis by $\mathbf{TS4}_{\mathbf{T1}}$ displaying a C−C bond breaking distance of 2.17 Å (calculated $\Delta G^{\ddagger}$ = 13.3 kcal mol^{-1}) forms triplet-state intermediate $\mathbf{2}_{\mathbf{T1}}$. Finally, relaxation to the ground state affords computed singlet-state $\mathbf{2}_{\mathbf{S1}}$ corresponding to product **2** (Scheme 3).

In solutions containing CH_3OH, a competent hydrogen atom donor,[13] radical $\mathbf{4}_{\mathbf{S1}}$, can be intercepted as reduced product **10**, offering us a "snapshot" of the reaction in progress (Scheme 4). In aqueous solutions, the reaction path is somewhat different. The biradical reacts as a zwitterion (suggesting a singlet state) with water in an overall photohydration.[14] In fact, irradiation in a mixture of MeCN/H_2O results in exclusive formation of alcohol **11** (Scheme 4). These results also bolster the hypothesis that the nitrile nitrogen atom (instead of hydrogen atoms) must intercept diradical $\mathbf{5}_{\mathbf{T1}}$.

■ CONCLUSION

We have chronicled an unusual photooxygenation reaction in stable *p*-QM **1**. Mechanistic details point to the criticality of the *p*-QM moiety, the excitation of an adjacent aromatic ring, diradical intermediates, and also to the indispensable nitrile

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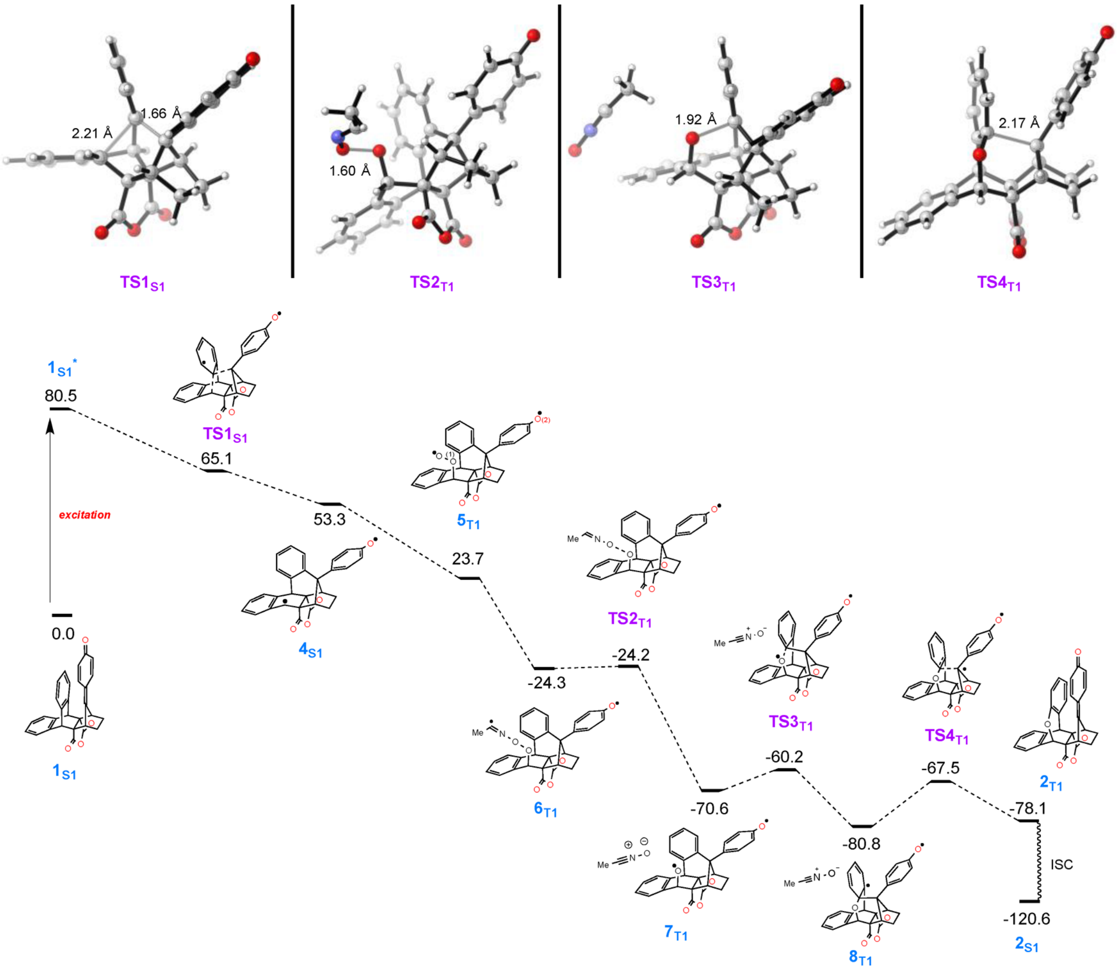
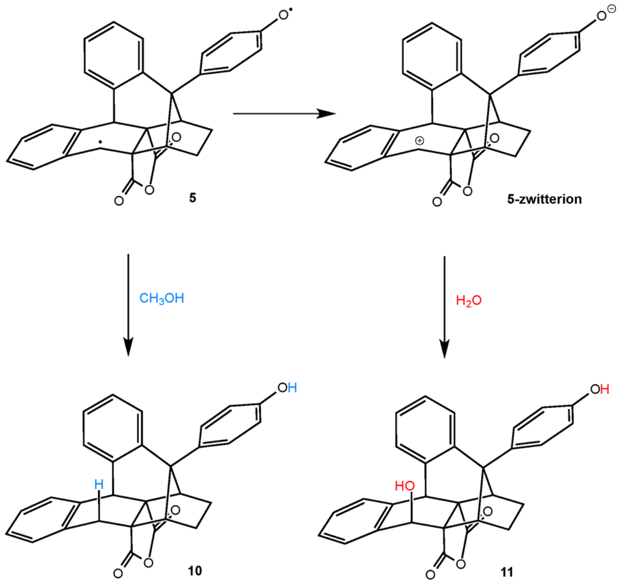
Scheme 3. Proposed Mechanism for Oxygen Insertion into 1



Scheme 4. Photoreduction and Photohydration Alternatives



solvent. Although fairly unique and complex, the results described herein may eventually point the way toward making oxygen insertions more general (e.g., the use of a stable, exogenous QM photocatalyst). Further investigations toward this goal are now underway.

■ EXPERIMENTAL SECTION

Synthesis of the *p*-QM (1). Compound **1** (*p*-QM) was synthesized following the previously reported method.[5]

Photooxygenated Product 2. *p*-QM **1** (74 mg, 0.17 mmol) was dissolved in 5 mL of CH_3CN and exposed to 254 nm light in a Rayonet reactor for 16 h. The solution was exposed to air through a needle for complete conversion (>90% yield by ^{1}H NMR). Solvent was evaporated under reduced pressure, and an analytical sample for characterization was obtained by MPLC as a yellow solid (27 mg, 0.06 mmol): ^{1}H NMR ($CDCl_3$) δ 7.31−7.38 (m, 4H), 7.22 (m, 1H), 7.05 (dd, 1H, *J* = 7.5 Hz, 1.7 Hz), 6.79 (m, 1H, *J* = 7.5 Hz, 1.7 Hz), 6.68 (m, 1H, *J* = 7. Five Hz, 1.3 Hz), 6.54 (m, 1H, *J* = 9.9 Hz, 2.5 Hz), 6.37 (m, 1H, *J* = 9.9 Hz, 1.9 Hz), 6.22 (m, 1H, *J* = 8.2 Hz, 1.13 Hz), 5.97 (m, 1H, *J* = 9.9 Hz, 2 Hz), 5.5 (s, 1H), 4.16 (s, 1H), 3.88 (d, 1H, *J* = 3.4 Hz), 3.45 (d, 1H, *J* = 3 Hz), 1.76−1.99 (m, 4H); ^{13}C NMR {^{1}H} ($CDCl_3$) δ 186.5, 172.4, 170.3, 163.8, 153.9, 140.2, 135.9, 135.5, 131.3, 130.9, 129.97, 129.5, 129.2, 129.1, 128.9, 128.6, 125.6, 123.3, 122.5, 122.2, 118.5, 63.8, 76.9, 62. 2, 49.4, 43.5, 43.3, 24.4, 24.1; IR 2979, 2930, 2895, 1850, 1780, 1636, 1582, 1487, 1453 (cm^{-1}, CaF_2, CH_2Cl_2); HRMS (ESI-Ion Trap) *m*/*z* $[M + Na]^+$ calcd for $C_{29}H_{20}O_5Na^+$ 471.120295, found 471.120208. (For $^{18}O_2$ insertion, HRMS (ESI-Ion Trap) *m*/*z* $[M]^-$ calcd for $C_{29}H_{20}O_4{}^{18}O^-$ 449.128043, found 449.128116.)

Photoreduction Product 10. Compound **1** (50 mg, 0.12 mmol) was dissolved in a mixture of 7 mL of CH_3CN and 1 mL of CH_3OH. The reaction vessel was purged with N_2 for 5 min, sealed under N_2 atmosphere, and then exposed to 254 nm light in a Rayonet reactor for 12 h. The solvent was removed under reduced pressure, and the reaction mixture was subjected to gradient column chromatography by MPLC. The photoreduced product **10** was isolated as the major product (18 mg, 0.04 mmol, 36% yield). Its characterization data were consistent with those reported in the literature.[5]

Photohydration Product 11. Compound **1** (95 mg, 0.22 mmol) was dissolved in a mixture of 7 mL of CH_3CN and 1 mL of H_2O. The reaction flask was then purged with N_2 for 5 min, sealed under N_2 atmosphere, and then exposed to 254 nm light in a rayonet reactor for 12 h. Solvents were removed under reduced pressure, and the product **11** was isolated by MPLC as white solid (45 mg, 0.1 mmol, 46% yield): ^1H NMR (CD_3CN) δ 7.62 (m, 1H, J = 7.5 Hz, 1 Hz), 7.44–7.51 (m, 2H), 7.35 (m, 1H, J = 7.5 Hz, 1.4 Hz), 7.25 (m, 1H, J = 7.5 Hz, 1 Hz), 7.05 (s, 1H), 6.92–7.01 (m, 5H), 6.8 (m, 1H, J = 8 Hz, 2.7 Hz), 6.57 (m, 1H, J = 7.8 Hz, 1 Hz), 4.95 (d, 1H, J = 9 Hz), 4.9 (s, 1H), 3.69 (m, 1H, J = 3.7 Hz, 1.25 Hz), 3.21 (m, 1H, J = 4.5 Hz, 1.3 Hz), 2 (m, 1H), 1.82 (m, 1H), 1.7 (m, 1H), 1.54 (d, 1H, J = 9 Hz), 1.39 (m, 1H); ^{13}C NMR {^1H} (DMSO-d_6) δ 175.9, 173.7, 156.3, 141.8, 140.7, 137.6, 135.8, 132.8, 130.92, 130.88, 130.7, 129.7, 129.6, 129.5, 128.6, 128.2, 126.0, 125.97, 116.3, 115.2, 71.2, 65.1, 63.8, 63.5, 50.2, 49.3, 44.95, 26.6, 22.8; IR 3574.5, 2362.7, 1846.5, 1780.3, 1735.5, 1611.8, 1515.7 (cm^{-1}, CaF_2, CH_2Cl_2); HRMS (ESI-Ion Trap) m/z [M + H]+ calcd for $C_{29}H_{23}O_5^+$ 451.15455, found 451.15326.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra, crystal structure data and computational information are included in the Supporting Information (available free of charge on the ACS Publications Web site). Crystal Structure for Compound **1** (CCDC 1897938) Crystal Structure for Compound **2** (CCDC 1946234) The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b02238.

NMR spectra, crystal structure data, and computational information (PDF)

Crystal structure for compound **1** (CIF)

Crystal structure for compound **2** (CIF)

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Notes

The authors declare no competing financial interest.

X-ray crystallographic data for compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre.

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