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Ground-state dioxygen undergoes metal-free [3 + 2]-annulations with allenes and nitrosoarenes under ambient conditions[†]

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The cycloadditions of molecular dioxygen with neutral π -bond motifs rely heavily on singlet-state ${}^{1}O_{2}$, whereas ground state ${}^{3}O_{2}$ is chemically inactive. Here we report novel [3 + 2]-annulations among ground-state ${}^{3}O_{2}$ (1 bar), allenes, and nitrosoarenes at low temperatures, efficiently yielding dioxygen-containing oxacycles. With less hindered 1-arylallene derivatives, these dioxygen species undergo skeletal rearrangement to 3-hydroxy-1-ketonyl-2-imine oxides. These cycloadditions represent valuable one-pot *O*,*N*,*O*-trifunctionalizations of allenes. Our EPR experiments confirm the presence of 1,4-diradical intermediates from an allene/nitrosoarene mixture, which manifest the hidden diradical properties of nitrosoarenes.

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Introduction

Cycloadditions of two or three π -bond molecules are powerful tools to access carbo- or heterocycles. Ground-state ³O₂ has lowlying LUMO orbitals, but its triplet state greatly reduces its chemical reactivity toward neutral molecules1 unless a metal catalyst is present. The cycloadditions of ³O₂ dioxygen rely nearly exclusively on prior photo-activation to form singlet-state ${}^{1}O_{2}$ (ref. 1) that reacts with dienes,² olefins³ or even arenes⁴ in [n + 2]-cycloadditions (n = 2 and 4, Scheme 1, eqn (1)). This photolytic process requires a sensitizer in a cold bath $(-40 \ ^{\circ}C)$ over a protracted period (>12 h) because highly energetic ¹O₂ might produce byproducts from the oxygen-ene reactions⁵ and oxidative C=C cleavages.6 In the case of allenes, singlet dioxygen afforded complicated mixture of undesired а compounds.7a,b

As ground-state ${}^{3}O_{2}$ is a free π -molecule and is available everywhere; its metal-free [n + 2]-cycloadditions with commonly used unsaturated hydrocarbons would provide a clean and cheap synthesis of valuable 1,*n*-diols, although there is no literature precedence. As far as we are aware, only 1,4-diradical precursors such as *o*-benzocyclobutanes,⁸ 1,2,6,7-octatetraenes,⁹ 2,3-dimethylenebicyclo[2.2.0]hexane¹⁰ and other 1,4diazo species¹¹ reacted with ground-state ${}^{3}O_{2}$ in thermal [4 + 2]- cycloadditions; these precursors are too uncommon to show general utility. We recently achieved metal-catalyzed annulations of N-hydroxy allenylamines with nitrosoarenes via a single radical process.^{7d} In search of a breakthrough in dioxygen chemistry, we developed facile [3 + 2]-cycloadditions among nitrosoarenes, allenes and ground-state ³O₂ to efficiently afford N-(1,2-dioxolan-4-ylidene)aniline oxides (eqn (2)). Particularly notable are the ambient conditions: -15 to 0 °C, ${}^{3}O_{2}$ (1 bar), no light, no catalyst and no additive. Importantly, these facile spinforbidden dioxygen annulations reveal a new role of nitrosoarenes as effective diradical precursors that is synthetically significant in nitroso chemistry.12 In the context of nitroso/ alkene and nitroso/alkyne reactions,13 theoretical calculations by Houk^{12e,f} suggested the intermediacy of the diradical species, but these transient species could not be trapped with dioxygen or other small molecules.

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Scheme 1 Cycloadditions of unsaturated hydrocarbons with ${}^{1}O_{2}$ and ${}^{3}O_{2}$.

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Fig. 1 *O,N,O*-Trifunctionalizations of allenes and selected natural products.

2-Amino-1,3-diols are present in numerous natural products with diverse biological activity (Fig. 1).¹⁴ Catalytic *O*,*N*,*O*-tri-functionalization of allenes is a new appealing tool to assess these motifs, as noted by the work of Schomaker, who reported Rh-catalyzed intramolecular cyclizations of homo-allenylsulfamate esters *via* a two-step sequence.^{15a} In contrast, our one-pot intermolecular *O*,*N*,*O*-functionalizations employ common and cheap nitrosoarenes, allenes and oxygen.

Results and discussion

Table 1 presents the optimized yields of a O,N,O-trifunctionalized molecule **3a** from a mixture of allene **1a**, nitrosobenzene **2a** (*n* equiv.) and O_2 (1 bar). When 1.5 equiv. of nitrosobenzene **2a** was used in cold THF (-15 °C), the yield was 43% (entry 1). The yield of **3a** increased to 63% with nitrosobenzene in three fold proportions (entry 2). In other solvents, the yields of **3a** were 50% in toluene, 54% in CH₃CN, and 58% in DCM (entries 3–5). The yield of **3a** decreased substantially to 10% in THF at 25 °C (entry 6). The reaction under N₂ failed to yield the desired product **3a** in a traceable amount (entry 7).¹⁶ Compound **3a** assumes an E-configuration with its hydroxyl *cis* to the nitrone oxygen to form a hydrogen bond. This structure was inferred from X-ray diffraction measurements of its relative **3b**¹⁷ (Table 2 entry 1).

| Table 1 | Optimization | of reaction | conditions |
|---------|--------------|-------------|-------------|
| Table 1 | opunization | orreaction | contaition. |

| Ph 1a | + N.O 2a n eq. | gas (1 atm) temp, time solvent | Ph O Ph Ph N O H O H O H O H O H D H O H D H C C C C C C C C C C C C C |
|----------|----------------------|--------------------------------------|---|
|----------|----------------------|--------------------------------------|---|

| Entry | Solvent ^a | Gas | n | $T(^{\circ}C)$ | <i>t</i> (h) | Yield ^b (% |
|-------|----------------------|---------------|-----|----------------|--------------|-----------------------|
| 1 | THF | 0, | 1.5 | -15 | 2 | 43 |
| 2 | THF | 0, | 3 | -15 | 2 | 63 |
| 3 | Toluene | $\tilde{O_2}$ | 3 | -15 | 2 | 50 |
| 4 | MeCN | $\tilde{O_2}$ | 3 | -15 | 2 | 54 |
| 5 | DCM | O_2 | 3 | -15 | 2 | 58 |
| 6 | THF | O_2 | 3 | 25 | 2 | 10 |
| 7 | THF | N_2 | 3 | -15 | 10 | _ |
| | | | | | | |

a [1a] = 0.1 M. b Product yields are reported after purification using a silica column.

 Table 2
 O,N,O-Trifunctionalizations of allenes with O2 and ArNO^{a,b}



 $^a\left[1 \right] = 0.1$ M. b Product yields are reported after purification using a silica column.

To assess the reaction scope, we applied these optimized conditions to additional mono- and 1,3-disubstituted allenes **1b-1g**; Table 2 summarizes the results. For phenylallene **1a**, its corresponding reactions with 4-methyl-, 4-methoxy- and 3,5-dimethylphenylnitroso species afforded 3-hydroxy-1-ketonyl-2-imine oxides **3b-3d** in 54–68% yields (entries 1–3). Varied arylallenes **1b-1e** (Ar = 4-MeC₆H₄, 4-ClC₆H₄, 4-BrC₆H₄ and 3-thienyl) yielded desired compounds **3e-3h** in satisfactory yields (50–74%, entries 4–6). 3-Substituted phenylallenes **1f** and **1g** (R = *n*-Bu and Ph) were also effective substrates for these cycloadditions (entries 8–10).

Notably, the reaction of sterically hindered 3-cyclohexyl-1phenylallene **1i** with 4-methoxyphenylnitroso **2c** and O₂ (1 bar) afforded dioxygen-containing oxacycle **4a** together with desired product **3l**; the yields were 45% and 28%, respectively. Species **4a** assumes an anti-configuration (dr > 20 : 1) according to its ¹H NOE spectra; this new compound was efficiently converted to compound **3l** in hot THF (eqn (3)), *via* a Kornblum– DeLaMare rearrangement.²²



The kinetic stability of dioxygen-containing oxacycle **4a** is enhanced with a suitable steric environment. We further tested the reactions on various 1-aryl-1-methylallenes **1j–1m** with 4methoxyphenylnitroso **2c** and O₂ (1 bar) in THF (0 °C), generating dioxygen-containing compounds **4b–4e** (Ar = 4-RC₆H₄, R = H, Me, MeO, Br) in satisfactory yields (Table 3, entries 1–4). The molecular structure of compound **4b** was confirmed by its X-ray

Table 3 [3 + 2]-Cycloadditions among O_2 , allenes and nitrosoarenes^{*a,b*}



 a^{a} [1] = 0.1 M. b^{b} Product yields are reported after purification using a silica column.

diffraction pattern.¹⁷ Various 1-aryl-3,3-dimethylallenes **1n–1q** (Ar = 4-RC₆H₄, R = H, Me, MeO, Br), electron-rich nitrosoarenes and O₂ were also amenable to such cycloadditions, yielding desired compounds **4f–4m** in satisfactory yields (60–72%, entries 5–12) except **4k** in only 38% yield. This dioxygen cycloaddition was applicable to cyclohexylidene-derived phenylallene **1r**, affording compound **4n** in 66% yield (entry 13). Compounds **4** serve as the first examples of the cycloadditions of ground-state ${}^{3}O_{2}$ with unsaturated hydrocarbons at low temperatures.

An electron-deficient nitrosoarene is an inapplicable substrate, as shown by eqn (4). Under O_2 , the reaction of trisubstituted allene **1p** with 4-chlorophenylnitroso species **2f** in cold THF (0 °C) afforded nitroso-containing cycloadduct **5a** in 53% yield; the dioxygen-containing product, *ca.* 5%, was unstable for isolation (eqn (4)). In contrast, the same allene **1p** could deliver dioxygen-containing species **4j** and **4k** using electron-rich nitrosoarenes under the same conditions (entries 9–10, Table 3).





 a [1] = 0.1 M. b Product yields are reported after purification using a silica column.

Under nitrogen, trisubstituted allene **1p** reacted with 4methylphenylnitroso **2b** in cold THF to form nitroso-containing cycloadduct **5b** in 60% yield (eqn (5)). The stereochemistry and its E-configuration of this new compound was confirmed by its X-ray diffraction pattern.¹⁷ Such a new reaction represents a new and useful *O*,*N*,*N*-functionalization of allenes. A preliminary survey of the reaction scope is summarized in Table 4. We tested the reactions on 1,3-di- and 1,1,3-trisubstituted allenes **1g** and **1t** that reacted with nitroso-arenes (R = H, Cl, CO₂Et) to afford nitroso-containing cycloadducts **5c–5g** in reasonable yields (58– 83%). Furthermore, the anti-configuration of compound **5c** was determined by X-ray diffraction.¹⁷

Dioxygen-containing heterocycles 4 are readily reduced with Pd/C, H₂ (1 atm) in MeOH (23 $^{\circ}$ C)¹⁸ to cleave their O–O bonds, satisfactorily yielding desired 1,3-dihydroxy-2-imine oxides 6. These reductions highlight the utility of molecular oxygen to afford 1,3-dihydroxy-2-amino derivatives. Several instances of affording tertiary 1,3-alcohol derivatives are illustrated in eqn (6) and (7); their chemical yields exceed 65%. Under these reductions, the valuable nitrone functionalities of these acyclic 1,3-diols remain intact as indicated by their HRMS and ¹³C-NMR spectra.





The facile cycloadditions among allenes, nitrones and ground-state O2 are very astonishing because an intersystem crossing (ISC) must be involved for one key intermediate. To investigate the mechanism, we examined the reaction of 1phenyl-3-cyclopropylallene 1s with 4-methylphenylnitroso species 2b under O₂, yielding compound 3m in 71% yield; this transformation did not induce cyclopropane cleavage because of the stability of the phenylallylic radical A (eqn (8)).¹⁹ We thus exclude the intermediacy of the dicarbon radical A', although analogous carbon radicals were postulated for the o-quinodimethine species.8 We isolated compound 7 in 13% yield from the reaction of 1-phenylallene 1a with PhNO (1.2 equiv.) and TEMPO (2 equiv.) under N₂, indicating the formation of diradical intermediates (eqn (9)). We employed EPR to characterize the diradical species from a mixture of 3,3-dimethyl-1phenylallene 1n and nitrosobenzene 2a in THF at 0 °C (0.5 h). Fig. 2 (top) shows the EPR signal of the diradical species; the intensity of this signal remains unchanged for 5 h under N₂. The simulation analysis was performed using the EasySpin program.20 The satisfactory fit was achieved with a twocomponent simulation (bottom). The abundant component (70%) corresponds to nitrogen-centered diradicals (g = 2.00616, $a_{\rm N} = 10.7$ G and 3.0 G).²¹ The minor component corresponds to a monoradical nitroxide with $a_{\rm N} = 10.7$ G. Notably, when recorded at T < 130 K, the spectrum exhibits a well-known nitroxide rigid-limit lineshape in accordance with the above simulation result; the coupling of unpaired electrons with the nitrogen center is evident.



Scheme 2 depicts a plausible mechanism to rationalize the remarkable facility of such dioxygen annulations. We postulate



Scheme 2 A plausible mechanism.

that allene 1 reacts initially with nitrosobenzene to form 1,4diradical species A, which is likely to be a major component, as detected in the EPR spectra; its nitroxy and allylic radicals are expected to couple with nitrogen in two magnitudes, *i.e.* $a_{\rm N} =$ 10.7 G and 3.0 G respectively.²¹ The capture of molecular dioxygen ³O₂ by 1,4-diradical species A forms peroxy diradical B in a triplet state, as the two radical centers of species B are remote from each other, rendering an intersystem crossing (ISC) feasible. After a change of spin state, singlet-state diradical B' is expected to form primary 1,2-oxaziridine diradical C through a 3-exo-trig cyclization that is more feasible than an alternative 5-endo-trig cyclization.23 A final radical-radical coupling of resulting species C forms precursor D, and ultimately yields desired 1,2-dioxolanes 4. This proposed path rationalizes the formation of compound 7 from the TEMPO experiment (eqn (9)) well. The trapping of the 1,4-biradical generates single radical species F that undergoes a rapid 3-exotrig cyclization to form benzylic radical G. A second trapping of this species with the TEMPO radical is expected to yield species I that is prone to hydrolysis on a silica column to yield observed product 7.

Conclusions

Prior to this work, singlet state oxygen ${}^{1}O_{2}$ failed to react with allenes to give useful oxygenated products.⁷ This study reports the first examples of metal-free [3 + 2]-cycloadditions among allenes, nitrosoarenes and ground-state ${}^{3}O_{2}$ (1 bar) at low temperatures, efficiently yielding dioxygen-containing oxacycles.²⁴ With less hindered 1-arylallene derivatives, the resulting oxacycles undergo skeletal rearrangement to 3-hydroxy-1-ketonyl-2-imine oxides. These transformations highlight a cheap, efficient and clean synthesis of 1,3-dihydroxy-2-amino derivatives. Our experimental data indicate that an initial attack of a nitrosoarene at an allene generates a diradical species that is detectable with EPR. We envisage that the concept of nitrosoarenes as diradical precursors will inspire new synthetic concepts.

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