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

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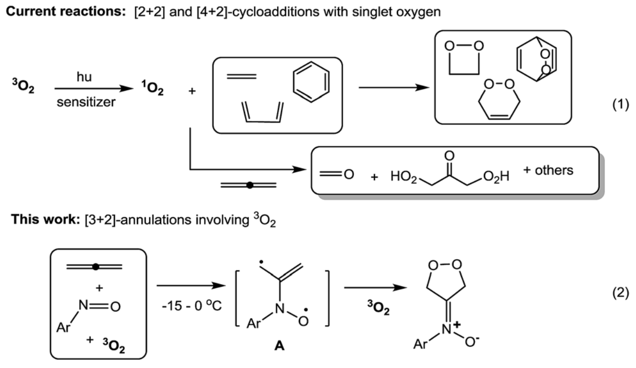
The cycloadditions of molecular dioxygen with neutral π-bond motifs rely heavily on singlet-state $^1O_2$, whereas ground state $^3O_2$ is chemically inactive. Here we report novel [3 + 2]-annulations among ground-state $^3O_2$ (1 bar), allenes, and nitrosoarenes at low temperatures, efficiently yielding 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.

Introduction

Cycloadditions of two or three π-bond molecules are powerful tools to access carbo- or heterocycles. Ground-state $^3O_2$ has low-lying LUMO orbitals, but its triplet state greatly reduces its chemical reactivity toward neutral molecules[1] unless a metal catalyst is present. The cycloadditions of $^3O_2$ dioxygen rely nearly exclusively on prior photo-activation to form singlet-state $^1O_2$ (ref. 1) that reacts with dienes,[2] olefins[3] or even arenes[4] in $[n + 2]$-cycloadditions ($n = 2$ and 4, Scheme 1, eqn (1)). This photolytic process requires a sensitizer in a cold bath (−40 °C) over a protracted period (>12 h) because highly energetic $^1O_2$ might produce byproducts from the oxygen-ene reactions[5] and oxidative C═C cleavages.[6] In the case of allenes, singlet dioxygen afforded a complicated mixture of undesired compounds.[7a,b]

As ground-state $^3O_2$ 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]hexane[10] and other 1,4-diazo species[11] reacted with ground-state $^3O_2$ 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 $^3O_2$ to efficiently afford *N*-(1,2-dioxolan-4-ylidene)aniline oxides (eqn (2)). Particularly notable are the ambient conditions: −15 to 0 °C, $^3O_2$ (1 bar), no light, no catalyst and no additive. Importantly, these facile spin-forbidden 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.



Scheme 1 Cycloadditions of unsaturated hydrocarbons with $^1O_2$ and $^3O_2$.

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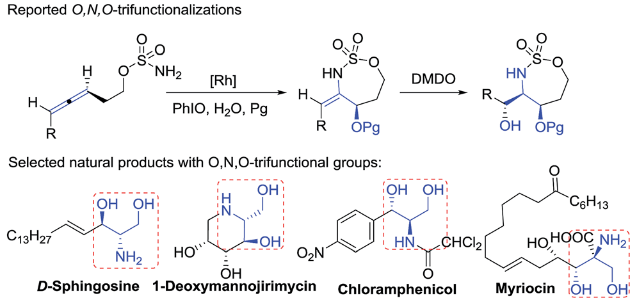


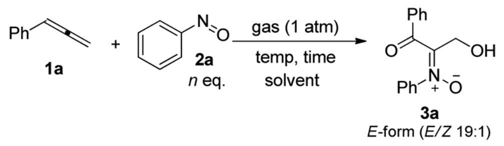
Fig. 1 *O,N,O*-Trifunctionalizations of allenes and selected natural products.

2-Amino-1,3-diols are present in numerous natural products with diverse biological activity (Fig. 1).[14] Catalytic *O*,*N*,*O*-trifunctionalization 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 homoallenylsulfamate 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 CH_3CN, 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 N_2 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).

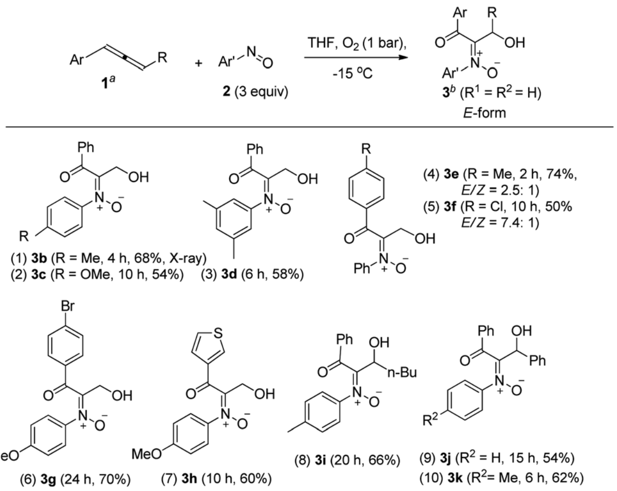
Table 1 Optimization of reaction conditions



Entry	Solvent[a]	Gas	*n*	*T* (°C)	*t* (h)	Yield[b] (%)
1	THF	O_2	1.5	−15	2	43
2	THF	O_2	3	−15	2	63
3	Toluene	O_2	3	−15	2	50
4	MeCN	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 O_2 and ArNO[a,b]

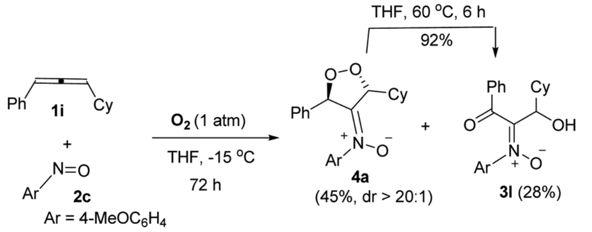


(1) **3b** (R = Me, 4 h, 68%, X-ray)
(2) **3c** (R = OMe, 10 h, 54%)
(3) **3d** (6 h, 58%)
(4) **3e** (R = Me, 2 h, 74%, *E*/*Z* = 2.5: 1)
(5) **3f** (R = Cl, 10 h, 50% *E*/*Z* = 7.4: 1)
(6) **3g** (24 h, 70%)
(7) **3h** (10 h, 60%)
(8) **3i** (20 h, 66%)
(9) **3j** (R^2 = H, 15 h, 54%)
(10) **3k** (R^2= Me, 6 h, 62%)

[a] [**1**] = 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-MeC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4 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-1-phenylallene **1i** with 4-methoxyphenylnitroso **2c** and O_2 (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]



(3)

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 4-methoxyphenylnitroso **2c** and O_2 (1 bar) in THF (0 °C), generating dioxygen-containing compounds **4b–4e** (Ar = 4-RC_6H_4, 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

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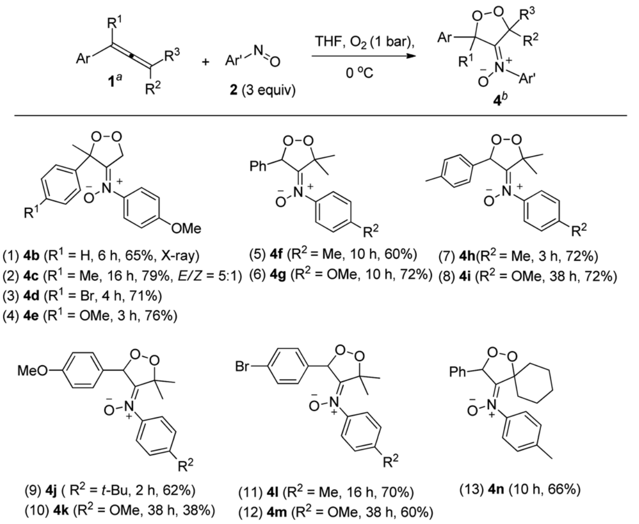
Table 3 [3 + 2]-Cycloadditions among O_2, allenes and nitrosoarenes[a,b]

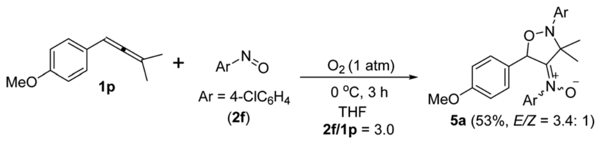


(1) **4b** (R^1 = H, 6 h, 65%, X-ray)
(2) **4c** (R^1 = Me, 16 h, 79%, E/Z = 5:1)
(3) **4d** (R^1 = Br, 4 h, 71%)
(4) **4e** (R^1 = OMe, 3 h, 76%)
(5) **4f** (R^2 = Me, 10 h, 60%)
(6) **4g** (R^2 = OMe, 10 h, 72%)
(7) **4h** (R^2 = Me, 3 h, 72%)
(8) **4i** (R^2 = OMe, 38 h, 72%)
(9) **4j** (R^2 = t-Bu, 2 h, 62%)
(10) **4k** (R^2 = OMe, 38 h, 38%)
(11) **4l** (R^2 = Me, 16 h, 70%)
(12) **4m** (R^2 = OMe, 38 h, 60%)
(13) **4n** (10 h, 66%)

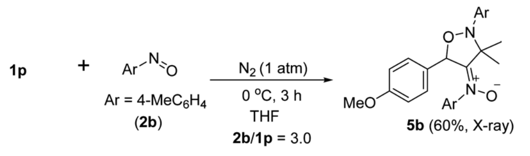
[a] [**1**] = 0.1 M. [b] Product yields are reported after purification using a silica column.

diffraction pattern.[17] Various 1-aryl-3,3-dimethylallenes **1n–1q** (Ar = 4-RC_6H_4, R = H, Me, MeO, Br), electron-rich nitrosoarenes and O_2 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 $^3O_2$ 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).

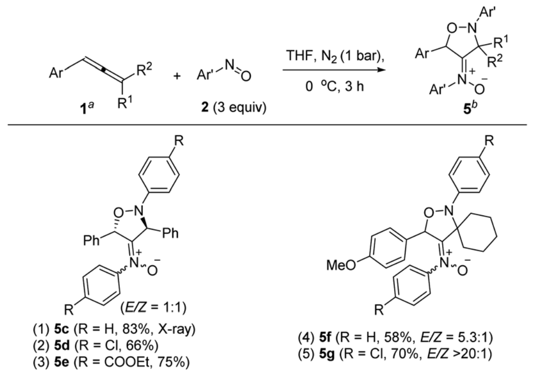


5a (53%, E/Z = 3.4: 1) (4)



5b (60%, X-ray) (5)

Table 4 [3 + 2]-Cycloadditions among allenes and nitrosoarenes under N_2[a,b]

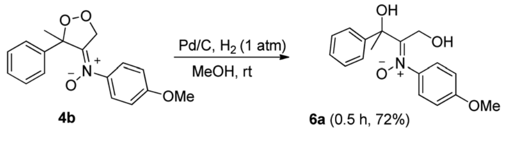


(1) **5c** (R = H, 83%, X-ray) (E/Z = 1:1)
(2) **5d** (R = Cl, 66%)
(3) **5e** (R = COOEt, 75%)
(4) **5f** (R = H, 58%, E/Z = 5.3:1)
(5) **5g** (R = Cl, 70%, E/Z >20:1)

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

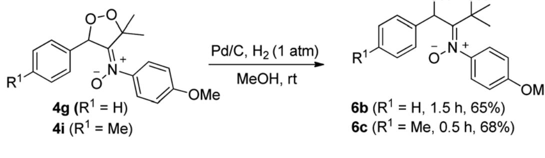
Under nitrogen, trisubstituted allene **1p** reacted with 4-methylphenylnitroso **2b** in cold THF to form nitroso-containing cycloadduct **5b** in 60% yield (eqn (5)). The stereochemistry and its E-configuration of this new compound was confirmed by its X-ray diffraction pattern.[17] Such a new reaction 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, CO_2Et) 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, H_2 (1 atm) in MeOH (23 °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 ^{13}C-NMR spectra.



4b

6a (0.5 h, 72%) (6)



4g (R^1 = H)
4i (R^1 = Me)

6b (R^1 = H, 1.5 h, 65%)
6c (R^1 = Me, 0.5 h, 68%) (7)

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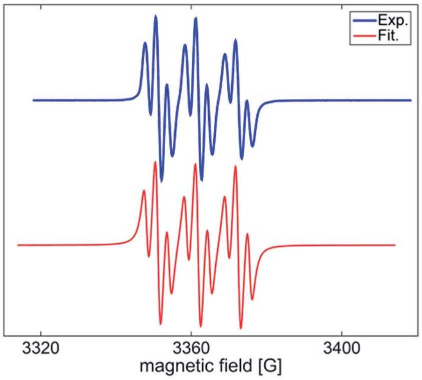
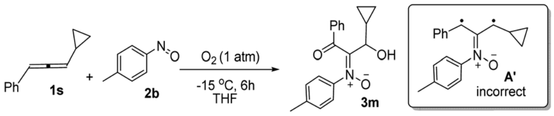
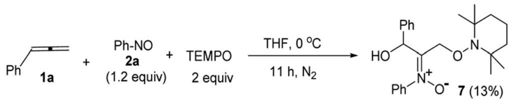


Fig. 2 Observed and simulated EPR spectra.

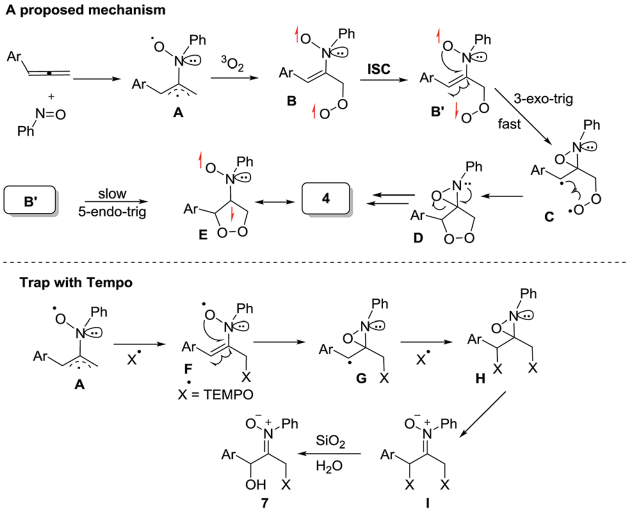
The facile cycloadditions among allenes, nitrones and ground-state O_2 are very astonishing because an intersystem crossing (ISC) must be involved for one key intermediate. To investigate the mechanism, we examined the reaction of 1-phenyl-3-cyclopropylallene **1s** with 4-methylphenylnitroso species **2b** under O_2, 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 N_2, indicating the formation of diradical intermediates (eqn (9)). We employed EPR to characterize the diradical species from a mixture of 3,3-dimethyl-1-phenylallene **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 N_2. The simulation analysis was performed using the EasySpin program.[20] The satisfactory fit was achieved with a two-component simulation (bottom). The abundant component (70%) corresponds to nitrogen-centered diradicals ($g = 2.00616$, $a_N = 10.7$ G and 3.0 G).[21] The minor component corresponds to a monoradical nitroxide with $a_N = 10.7$ 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.



(8)



(9)



Scheme 2 A plausible mechanism.

Scheme 2 depicts a plausible mechanism to rationalize the remarkable facility of such dioxygen annulations. We postulate that allene **1** reacts initially with nitrosobenzene to form 1,4-diradical 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.* $a_N = 10.7$ G and 3.0 G respectively.[21] The capture of molecular dioxygen $^3O_2$ 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-*exo-trig* 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 $^1O_2$ 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 $^3O_2$ (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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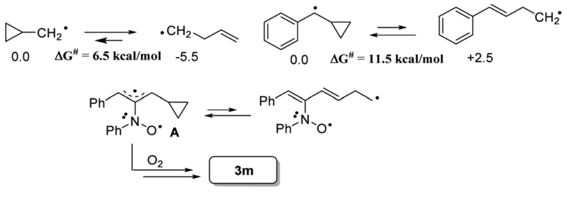

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