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

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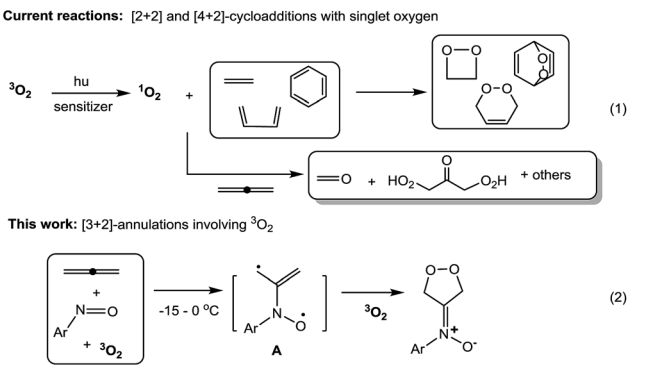
The cycloadditions of molecular dioxygen with neutral π-bond motifs rely heavily on singlet-state $^1O_2$, whereas ground state $^3O_2$ is chemically inactive. Here we report novel [3 + 2]-annulations among ground-state $^3O_2$ (1 bar), allenes, and nitrosoarenes at low temperatures, efficiently yielding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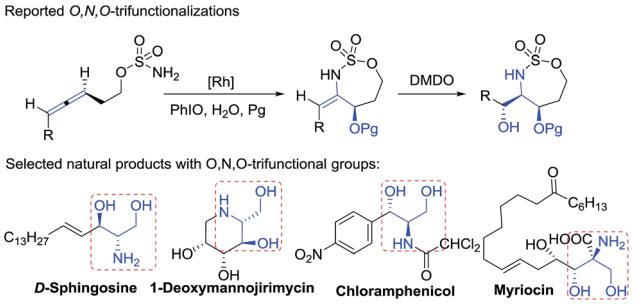


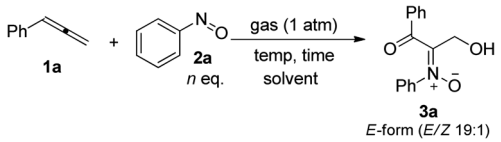
Fig. 1 *O,N,O*-Trifunctionalizations of allenes and selected natural products.

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).

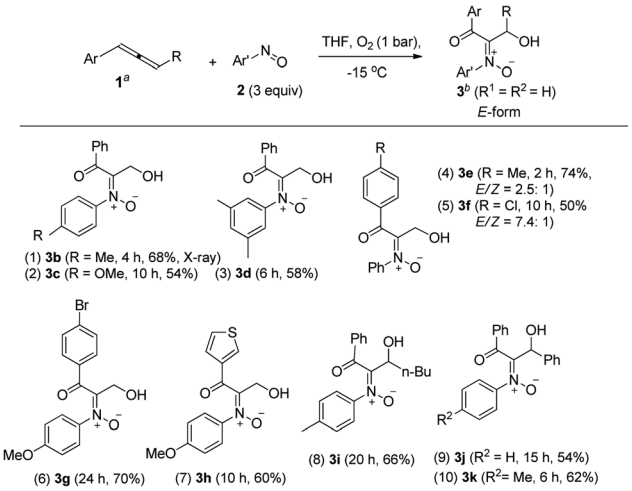
Table 1 Optimization of reaction conditions



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.

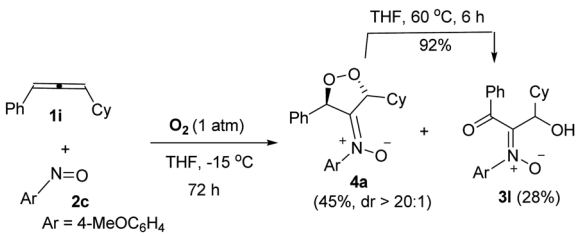
Table 2 *O,N,O*-Trifunctionalizations of allenes with O_2 and ArNO[a,b]



[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).

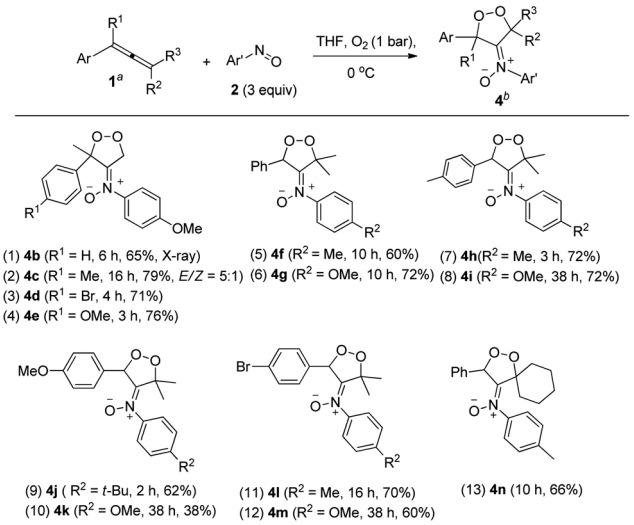
Notably, the reaction of sterically hindered 3-cyclohexyl-1-phenylallene **1i** with 4-methoxyphenylnitroso **2c** and O_2 (1 bar) afforded dioxygen-containing oxacycle **4a** together with desired product **3l**; the yields were 45% and 28%, respectively. Species **4a** assumes an anti-configuration (dr > 20 : 1) according to its ^{1}H 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

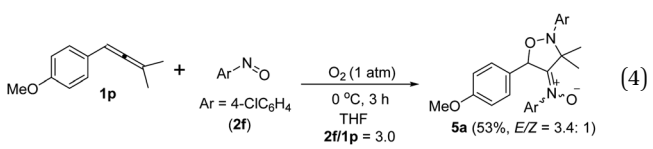
Table 3 [3 + 2]-Cycloadditions among O_2, allenes and nitrosoarenes[a,b]



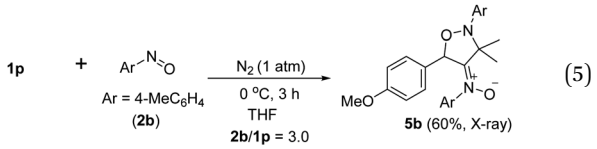
[a] [1] = 0.1 M. [b] Product yields are reported after purification using a silica column.

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).

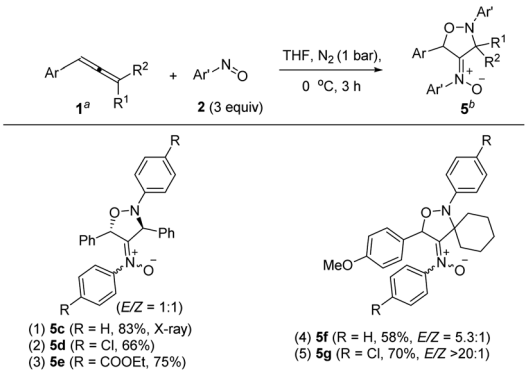


(4)



(5)

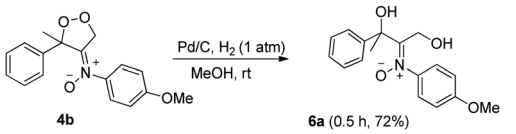
Table 4 [3 + 2]-Cycloadditions among allenes and nitrosoarenes under N_2[a,b]



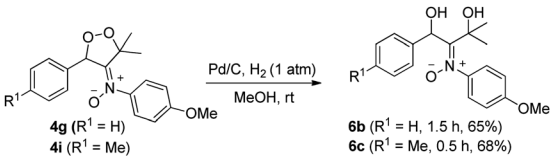
[a] [1] = 0.1 M. [b] Product yields are reported after purification using a silica column.

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.



(6)



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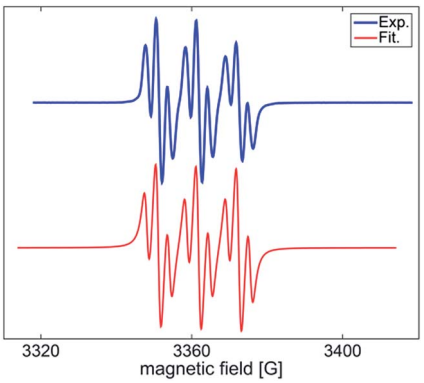
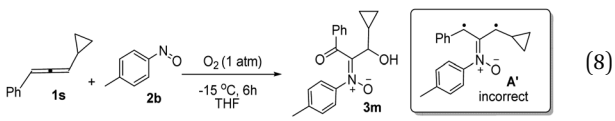
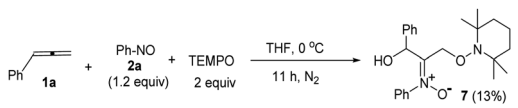


Fig. 2 Observed and simulated EPR spectra.

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.

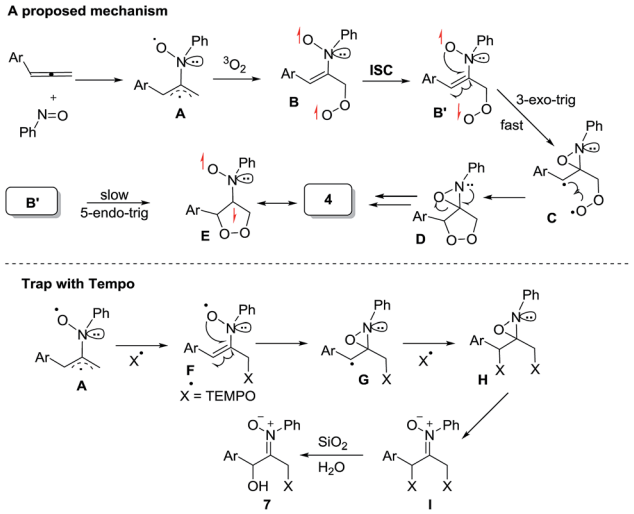


(8)



(9)

Scheme 2 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 1,4-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.

Acknowledgements

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Notes and references

1 For reviews see: (*a*) P. R. Ogilby, *Chem. Soc. Rev.*, 2010, **39**, 3181; (*b*) J. Sivaguru, M. R. Solomon, T. Poon, S. Jockusch, S. G. Bosio, W. Adam and N. Turro, *Acc. Chem. Res.*, 2008, **41**, 387; (*c*) A. Greer, *Acc. Chem. Res.*, 2006, **39**, 797; (*d*) A. G. Leach and K. N. Houk, *Chem. Commun.*, 2002, 1243.

2 (*a*) J. A. Celaje, D. Zhang, A. M. Guerrero and M. Selke, *Org. Lett.*, 2011, **13**, 4846; (*b*) E. Salamci, H. Seçen, Y. Sütbeyaz and M. Balci, *J. Org. Chem.*, 1997, **62**, 2453; (*c*) K. M. Davis and B. K. Carpenter, *J. Org. Chem.*, 1996, **61**, 4617.

3 (*a*) K. Ohkubo, T. Nanjo and S. Fukuzumi, *Org. Lett.*, 2005, **7**, 4265; (*b*) W. Adam, C. R. Saha-Moeller and S. B. Schambony, *J. Am. Chem. Soc.*, 1999, **121**, 1834; (*c*) K. A. Zaklika, B. Kaskar and A. P. Schaap, *J. Am. Chem. Soc.*, 1980, **102**, 386.

4 (*a*) M. Klaper and T. Linker, *Chem.–Eur. J.*, 2015, **21**, 8569; (*b*) W. Fudickar and T. Linker, *J. Am. Chem. Soc.*, 2012, **134**, 15071; (*c*) H. Kotani, K. Ohkubo and S. Fukuzumi, *J. Am. Chem. Soc.*, 2004, **126**, 15999.

5 (*a*) A. Eske, B. Goldfuss, A. G. Griesbeck, A. Kiff, M. Kleczka, M. Leven, J.-M. Neudorfl and M. Vollmer, *J. Org. Chem.*, 2014, **79**, 1818; (*b*) W. Adam and M. J. Richter, *J. Org. Chem.*, 1994, **59**, 3335; (*c*) L. M. Stephenson, *Acc. Chem. Res.*, 1980, **13**, 419.

6 W. Adam and H. Rebollo, *Tetrahedron Lett.*, 1981, **22**, 3049.

7 (*a*) K. Gollnick and A. Schnatterer, *Tetrahedron Lett.*, 1985, **26**, 5029; (*b*) I. Erden and T. R. Martinez, *Tetrahedron Lett.*, 1991, **32**, 1859; (*c*) R. K. Howe, *J. Org. Chem.*, 1968, **33**, 2848; (*d*) P. Sharma and R. S. Liu, *Org. Lett.*, 2016, **18**, 412.

8 (*a*) J. Drujon, R. Rahmani, V. Heran, R. Blanc, Y. Carissan, B. Tuccio, L. Commeiras and J. Parrain, *Phys. Chem. Chem. Phys.*, 2014, **16**, 7513; (*b*) W. R. Roth, T. Ebbrecht and A. Beitat, *Chem. Ber.*, 1988, **121**, 1357.

9 (*a*) W. R. Roth, R. Longer, M. Bartmann, B. Stevermann, G. Maier, H. P. Reisenauer, R. Sustmann and W. Müller, *Angew. Chem., Int. Ed.*, 1987, **26**, 256; (*b*) W. R. Roth, B. P. Scholz, R. Breuckmann, K. Jelich and H. W. Lennartz, *Chem. Ber.*, 1982, **115**, 1934.

10 W. R. Roth and B. P. Scholz, *Chem. Ber.*, 1982, **115**, 1197.

11 (*a*) W. Adam, S. Grabowski and H. Platsch, *J. Am. Chem. Soc.*, 1989, **111**, 751; (*b*) W. Adam, K. Hannemann and R. M. Wilson, *J. Am. Chem. Soc.*, 1986, **108**, 929; (*c*) W. Adam, K. Hannemann and R. M. Wilson, *J. Am. Chem. Soc.*, 1984, **106**, 1646; (*d*) W. R. Roth, M. Biermann, G. Erker, K. Jelich, W. Gerhartz and H. Görner, *Chem. Ber.*, 1980, **113**, 586.

12 (*a*) H. Yamamoto and N. Momiyama, *Chem. Commun.*, 2005, 3514; (*b*) W. Adam and O. Krebs, *Chem. Rev.*, 2003, **103**, 4131; (*c*) P. Zuman and B. Shah, *Chem. Rev.*, 1994, **94**, 1621; (*d*) K. Mikami and M. Shimizu, *Chem. Rev.*, 1992, **92**, 1021; (*e*) A. G. Leach and K. N. Houk, *Org. Biomol. Chem.*, 2003, **1**, 1389; (*f*) A. G. Leach and K. N. Houk, *J. Am. Chem. Soc.*, 2002, **124**, 14820; (*g*) D. J. Fisher, G. L. Burnett, R. Velasco and J. R. de Alaniz, *J. Am. Chem. Soc.*, 2015, **137**, 11614.

13 (*a*) G. Ieronimo, A. Mondelli, F. Tibiletti, A. Maspero, G. Palmisano, S. Galli, S. Tollari, N. Masciocchi, K. M. Nicholas, S. Tagliapietra, G. Cravotto and A. Penoni, *Tetrahedron*, 2013, **69**, 10906; (*b*) A. Penoni, G. Palmisano, Y. L. Zhao, K. N. Houk, J. Volkman and K. M. Nichols, *J. Am. Chem. Soc.*, 2009, **131**, 653.

14 (*a*) M. Kurano, K. Tsukamoto, M. Hara, R. Ohkawa, H. Ikeda and Y. Yatomi, *J. Biol. Chem.*, 2015, **290**, 2477; (*b*) E. Ogier-Denis, A. Blais, J. J. Houri, T. Voisin, G. Trugnan and P. Codogno, *J. Biol. Chem.*, 1994, **269**, 4285; (*c*) O. N. Kostopoulou, E. C. Kouvela, G. E. Magoulas, T. Garnelis, I. Panagoulias, M. Rodi, G. Papadopoulos, A. Mouzaki, G. P. Dinos, D. Papaioanmou and D. L. Kalpaxis, *Nucleic Acids Res.*, 2014, **42**, 8621; (*d*) E. N. Glaros, W. S. Kim, B. J. Wu, C. Suarna, C. M. Quinn, K.-A. Rye, R. Stocker, W. Jessup and B. Garner, *Biochem. Pharmacol.*, 2007, **73**, 1340.

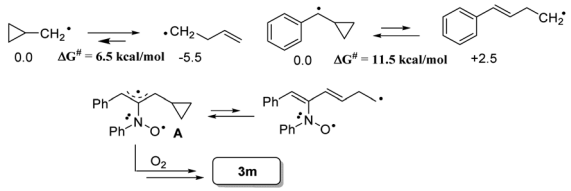
15 Triple functionalizations of allenes are focused extensively on their double epoxidations,[15c–e] and other reactions are very few.[15a,b] See: (*a*) C. S. Adams, R. D. Grigg and J. M. Schomaker, *Chem. Sci.*, 2014, **5**, 3046; (*b*) W. Zhao and J. Montgomery, *J. Am. Chem. Soc.*, 2016, **138**, 9763; (*c*) C. S. Adams, C. D. Weatherly, E. G. Burke and J. M. Schomaker, *Chem. Soc. Rev.*, 2014, **43**, 3136; (*d*) S. D. Lotesta, S. Kiren, R. R. Sauers and L. J. Williams, *Angew. Chem., Int. Ed.*, 2007, **46**, 7108; (*e*) P. Ghosh, S. D. Lotesta and L. J. Williams, *J. Am. Chem. Soc.*, 2007, **129**, 2438–2439.

16 R. K. Howe, *J. Org. Chem.*, 1968, **33**, 2848.

17 Crystallographic data of **3b**, **4b**, **5b** and **5c** were deposited at the Cambridge Crystallographic Data Centre (**3b** CCDC 1507478, **4b** CCDC 1507477, **5b** CCDC 1510902, **5c** CCDC 1540299).

18 T. V. Robinson, D. S. Pedersen, D. K. Taylor and R. T. Tiekink, *J. Org. Chem.*, 2009, **74**, 5093.

19 The rearrangement of cyclopropylmethyl radicals to homoallylic radicals is seriously affected by the radical substituents; this process is reversible. Previous studies by Bowry indicate that stable cyclopropylbenzylic radicals are reluctant to form the corresponding homoallylic radicals. In our system, key intermediate **A** is a very stable phenylallylic radical that has many resonance forms. The equilibrium of this rearrangement is expected to be favourable for initial radicals **A** that can be trapped by O_2 to yield the observed product **3m**. For the nature of this radical rearrangement, see the leading reference, A. J. Beckwith and V. W. Bowry, *J. Am. Chem. Soc.*, 1994, **116**, 2710–2716.



20 S. Stoll and R. D. Britt, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6614.

21 (*a*) L. Jonkman, H. Muller and J. Kommandeur, *J. Am. Chem. Soc.*, 1971, **93**, 5833; (*b*) V. Branchadell, J. Font, A. G. Moglioni, C. O. de Echagulen, A. Oliva, M. Rosa, R. M. Ortuno, J. Veciana and J. Vidal-Gancedo, *J. Am. Chem. Soc.*, 1997, **119**, 9992; (*c*) P. Astolfi, P. Carloni, E. Damiani, L. Greci, M. Marini, C. Rizzoli and P. Stipa, *Eur. J. Org. Chem.*, 2008, 3279.

22 (*a*) N. Kornblum and H. E. DeLaMare, *J. Am. Chem. Soc.*, 1951, **73**, 880; (*b*) S. T. Staben, X. Linghu and F. D. Toste, *J. Am. Chem. Soc.*, 2006, **128**, 12658.

23 (*a*) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734; (*b*) J. E. Baldwin, J. Cutting, W. Dupont, L. Kruse, L. Silberman and R. C. Thomas, *J. Chem. Soc., Chem. Commun.*, 1976, 736; (*c*) C. Chatgilialoglu, C. Ferreri, M. Guerra, V. Timokhin, G. Froudakis and T. Gimisis, *J. Am. Chem. Soc.*, 2002, **124**, 10765.

24 For metal-catalyzed oxidations of 5-hydroxy-1-enes with O_2 to yield tetrahydrofuran products, see (*a*) S. Inoki and T. Mukayama, *Chem. Lett.*, 1990, 67–70; (*b*) C. Palmer, N. M. Morra, A. C. Stevens, B. Bajtos, B. P. Machin and B. L. Pagenkopf, *Org. Lett.*, 2009, **11**, 5614–5617; (*c*) R. M. Trend, Y. K. Ramtohul, E. M. Ferreira and B. M. Stoltz, *Angew. Chem., Int. Ed.*, 2003, **42**, 2892; (*d*) X. Xie and S. S. Stahl, *J. Am. Chem. Soc.*, 2015, **137**, 3767; (*e*) S. L. Zultanski, J. Zhao and S. S. Stahl, *J. Am. Chem. Soc.*, 2016, **138**, 6416.