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Dirhodium caprolactamate and *tert*-butyl hydroperoxide – a universal system for selective oxidations

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Oxidations with *tert*-butyl hydroperoxide (TBHP) catalyzed by dirhodium caprolactamate [Rh_2(cap)$_4$] provide mild and selective protocols for the oxidative Mannich reaction, conversion of secondary amines to imines, dearomatization of 4-substituted phenols, and oxyfunctionalization of allylic, benzylic, and propargylic positions. The dirhodium catalyst in combination with TBHP is a convenient platform for mechanistic investigations, and their uses point to a variety of directions for the future evolution of the field.

Introduction

Oxidation reactions play an important role in biological systems and in industrial processes.[1–5] The search for precise control over the oxidation state of functional groups in target molecules and for chemo- and regioselectivity of oxidation has led to the development of a large variety of oxidative protocols. The desire to vary selectivity and improve efficiency has inspired progress in catalytic approaches, and cost has drawn investigators towards dioxygen as the optimal oxidant.[6–9] In efforts to provide oxidations by molecular oxygen, peroxides have been useful for the development of selective oxidations and for understanding how to eventually engage dioxygen. Both two-electron and one-electron transfer processes are known and well established, and peroxide chemistry has contributed greatly to the development of understanding of free radical processes.[1,4] Over the last 10 years,[10–12] Doyle and coworkers have achieved substantial progress in developing and understanding radical oxidations in their investigations of a general and selective oxidative system using dirhodium caprolactamate [Rh_2(cap)$_4$] as a catalyst and *tert*-butyl hydroperoxide (TBHP) as a terminal oxidant. This review will discuss current applications of this catalytic system and available mechanistic models as well as outline perspectives for its evolution.

A wide range of oxidative processes employs TBHP as a terminal oxidant.[1,13] With a half-life of over 520 h in refluxing benzene, TBHP has fewer handling risks than does H_2O_2 in water or peracetic acid.[14] The low acidity of TBHP (pK_a = 12.8) contributes to the versatility of its uses, and volatile reaction products derived from TBHP (*tert*-butyl alcohol, water, molecular oxygen, and di-*tert*-butyl peroxide) simplify purification. Anhydrous solutions of TBHP are commercially available or can be easily prepared due to the high solubility of TBHP in organic solvents. Furthermore, TBHP is available as a 70% aqueous solution (T-HYDRO) that offers fewer handling risks and is less expensive than solutions of TBHP in decane or benzene.

tert-Butyl hydroperoxide is a source of the *tert*-butylperoxy radical (Scheme 1, equation 1) which is the selective one-electron oxidant and is crucial to the versatility of TBHP applications. Suitable candidates for X are any chemical species for which the abstraction reaction is kinetically and thermodynamically feasible. However, common methods often generate the *tert*-butylperoxy radical indirectly. The initial step involves homolytic cleavage of the oxygen–oxygen bond that yields the highly reactive and unselective *tert*-butoxy radical (equation 2) followed by hydrogen atom abstraction from TBHP by the *tert*-butoxy radical

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Michael P. Doyle received his B.S. degree from the College of St. Thomas in St. Paul, MN, and obtained his Ph.D. degree from Iowa State University. Following a postdoctoral engagement at the University of Illinois at Chicago, he joined the faculty at Hope College in 1968, moved in 1964 to Trinity University in San Antonio, TX, and in 1997 came to Tucson, AZ, as Vice President, then President, of Research Corporation and Professor of Chemistry at the University of Arizona. He moved to the University of Maryland as Professor and department chair in 2003. He has been the recipient of numerous national awards, including the George C. Pimentel Award for Chemical Education (2002) and the Arthur C. Cope Scholar Award (2006) from the American Chemical Society, and he has been honored to be named Doctor Honoris Causa of the Russian Academy of Sciences (1994). He has written or coauthored eleven books, 22 book chapters, and he is the co-author of more than 330 journal publications in the areas of chemical oxidations, asymmetric catalysis, metal carbene chemistry, bioinorganic nitrosyl chemistry, and organosilane reductions. He serves on the editorial boards of three research journals and *Chemical & Engineering News*.

$$X + Bu^tOOH \longrightarrow X–H + Bu^tOO^\bullet \quad (1)$$

$$Y + Bu^tOOH \longrightarrow Y–OH + Bu^tO^\bullet \quad (2)$$

$$Bu^tO^\bullet + Bu^tOOH \longrightarrow Bu^tOH + Bu^tOO^\bullet \quad (3)$$

Scheme 1

(equation 3) at a nearly diffusion controlled rate.[15] The candidates for Y include Lewis acids that can bind the hydroxyl group of TBHP and are one-electron reductants capable of oxygen–oxygen bond cleavage. The conversion of Y–OH back to Y is the major challenge of the development of the catalytic processes based on TBHP. And although many transition metal complexes[1,16–27] and inorganic salts[13,28–33] exhibit this catalytic activity in oxidative transformations with TBHP, dirhodium caprolactamate achieves the highest turnover numbers.[34]

Applications of *tert*-butyl hydroperoxide in oxidative reactions often achieve (a) greater selectivities than those achieved from reactions with hydrogen peroxide[35] and (b) higher reaction rates than those achieved with cumyl hydroperoxide or dioxygen.[36–40] Synthetic applications of TBHP include epoxidation,[41–44] carbon–carbon double bond oxidations,[39,45,46] oxidation of non-activated C–H bonds,[35,47,48] formation of internal peroxides,[36,49–51] and polymerization.[52,53] In the presence of $Rh_2(cap)_4$, TBHP enables selective allylic oxidations of steroidal[54–56] and cyclic,[12] as well as electron-poor, acyclic alkenes,[54] benzylic oxidations,[57] propargylic oxidations,[58] oxidations of 4-substituted phenols,[34] aniline oxidations,[34] oxidative Mannich reactions of *N*,*N*-dialkylanilines,[11,59] and conversions of secondary amines to imines.[60] The mild conditions for oxidations with TBHP catalyzed by $Rh_2(cap)_4$ are suitable for tandem processes such as phenol oxidation – Michael addition,[61] hydroxylamine oxidation – hetero-Diels–Alder reaction,[62] and *N*,*N*-dialkylaniline oxidation – [3+2] cycloaddition.[63]

Allylic oxidation of cholesteryl acetate **1** offers a general example for a direct comparison of different catalysts in oxidations with TBHP (Table 1). The presence of stoichiometric amounts of sodium chlorite and hypochlorite (entries 1, 2) furnishes moderate yields, presumably, due to competing chlorination of **1**.[31,32] Copper(I) and trimanganese catalytic systems require respectively 68 and 10 mol% of catalyst that is not recycled (entries 3, 5). Reliance on TBHP solution in decane puts $Mn_3O(OAc)_3$, $BiCl_3$, CuI, and $Co(OAc)_2$ catalytic systems (entries 3, 4, 6, 7) at a disadvantage relative to catalysts that work with safe and inexpensive T-HYDRO. Furthermore, $BiCl_3$, CuI and $RuCl_3$ demand tenfold excess of TBHP (entries 4, 5, 8) that is undesirable for large scale reactions. Applications of immobilized dichromate (entry 9) are limited due to a high toxicity and carcinogenicity of chromium(VI) ions.[64] Iron(III) catalyzed oxidation of **1** by H_2O_2 (entry 10) furnishes only a 34% yield of enone and is accompanied by the presence of epoxide and alcohol by-products.[65] The data in Table 1 clearly indicate that $Rh_2(cap)_4$ is a superior catalyst due to higher yield, lower catalyst loading, and reliance on T-HYDRO for cholesteryl acetate oxyfunctionalization. Moreover, conclusions reached from this comparison are often suitable assessments for other oxidative transformations with TBHP.[11,34]

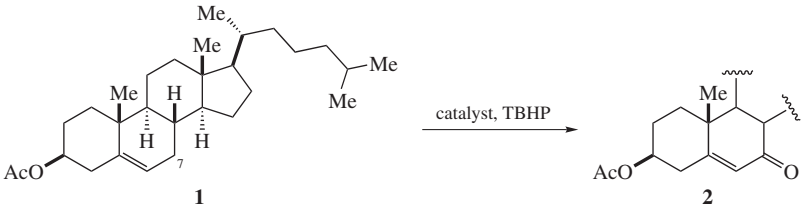
The exceptional catalytic activity of $Rh_2(cap)_4$ is determined by rapid reduction of the oxidized dirhodium(II,III) species formed by the process in equation (2)[69] coupled with the low oxidation potential of $Rh_2(cap)_4$ (11 mV *vs*. SCE)[11,59,70] that maintains an optimal flux of oxo-radical species throughout the reaction. Other dirhodium carboxamidates have higher oxidation potentials, including dirhodium acetamidate (150 mV *vs*. SCE).[70] Dirhodium caprolactamate, whose convenient synthesis from easily obtained rhodium acetate has been described in detail,[56] has solubility and stability characteristics that complement its low oxidation potential to render its uses optimal for applications. In metal carbene chemistry, $Rh_2(cap)_4$ is known to be a weaker Lewis acid than dirhodium acetate, causing a slower rate for dinitrogen loss from diazo compounds in the formation of rhodium carbene intermediates,[71] but this catalyst exhibits higher selectivity in intramolecular reactions of diazocarbonyl compounds.[70–72]

Applications

Oxyfunctionalization

Oxyfunctionalization of the allyl position of cycloalkenes was the first $Rh_2(cap)_4$ catalyzed oxidation with TBHP.[12] This process initially utilized an anhydrous TBHP solution in hexane because of the unwarranted anticipation that water could replace the carboxamidate ligands on dirhodium. Addition of just 0.5 equiv. of K_2CO_3 increased product yield to 80% and allowed further exploration of the scope of $Rh_2(cap)_4$-based methodology (Scheme 2). More than ten di- and tri-substituted cyclic alkenes were successfully converted to enones in yields 60–94%. The oxidation was selective for the methylene group at the 3-position of the unsaturated carbocycles. Cyclic alkenes bearing alkyl or electron-withdrawing groups readily underwent oxidation to β-substituted cyclic enones (Scheme 2). The allylic oxidation of

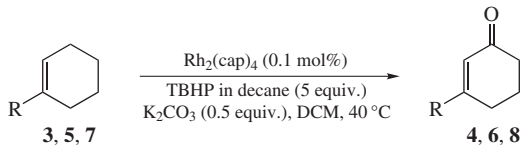
Table 1 Comparison of catalysts for cholesteryl acetate **1** oxidation with TBHP.



1 **2**

Entry	Catalyst/additive	Catalyst loading (mol%)	Oxidant	Equivalents of oxidant	*t*/h	*T*/°C	Yield (%)
1	$NaClO_2$	120	T-HYDRO	5	60	80	66[32]
2	NaOCl	200	T-HYDRO	6	10	2–5	68[31]
3	$Mn_3O(OAc)_3$	10	TBHP in decane	5	48	20	85[25]
4	$BiCl_3$	10	TBHP in decane	11	22	70	82[30]
5	$CuI/Bu_4N^+Br^-$	68/12	T-HYDRO	30	24	40	76[66]
6	CuI	2.6	TBHP in decane	7	24	70	80[67]
7	$Co(OAc)_2$ immobilized on silica	2.2	TBHP in decane	7	48	70	70[68]
8	$RuCl_3 \cdot H_2O$	0.7	T-HYDRO	10	24	20	75[26]
9	$Cr_2O_7^{2-}$ immobilized on SiO_2/ZrO_2	n/a	T-HYDRO	2	n/a	20	48[24]
10	Fe(picoline)$_3$	50	H_2O_2 (30% aq.)	5	3	20	34[65]
11	**$Rh_2(cap)_4$**	**1.0**	**T-HYDRO**	**5**	**20**	**40**	**80[55]**

cycloalkene was insensitive to the size of alkyl substituents, and 1-*tert*-butylcyclohexene furnished the corresponding enone in 94% (Scheme 2). A short plug of silica completely removes the dirhodium catalyst because the dirhodium(II,III) species that is formed in the oxidation process adheres strongly to the polar silica.

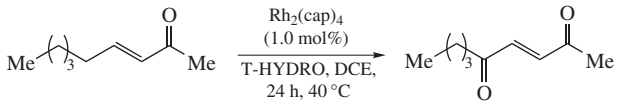


3, **5**, **7** **4**, **6**, **8**

Substrate	R	Product	*t*/h	Yield (%)
3	Bu^t	**4**	1	94
5	Ac	**6**	1	80
7	NO_2	**8**	24	62

Scheme 2

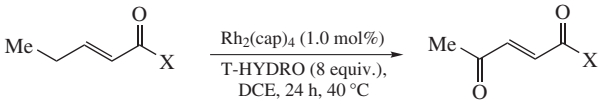
Further development of dirhodium catalyzed allylic oxidation led to the use of 70% aqueous solutions of TBHP (T-HYDRO)[54] in which ligand exchange on $Rh_2(cap)_4$ was limited. Applications of T-HYDRO eliminated the need for a basic additive that reduced potential unwanted base catalyzed oxo-Michael addition of hydroperoxide to enones.[1,43,73–77] Moreover, the new conditions enabled oxidation of acyclic alkenes bearing ketone and carboxylate groups (Schemes 3 and 4). However, because of the slower rate for hydrogen atom abstraction with enones, a tenfold excess of TBHP was critical to improve yield of a fire bee toxin **10**[78,79] (Scheme 3). Noteworthy, $Rh_2(cap)_4$ catalyzed allylic oxidation afforded, respectively, 82, 65 and 70% isolated yields of enediones bearing carboxylic acid and primary and secondary amides (Scheme 4).



9 **10**

Equiv. of T-HYDRO	Yield (%)
8	76
10	84

Scheme 3



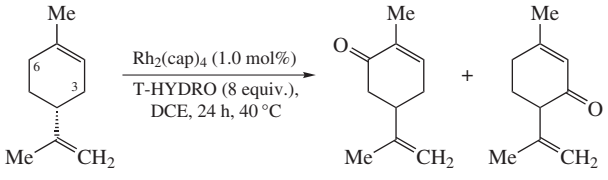
11, **13**, **15** **12**, **14**, **16**

Substrate	X	Product	Yield (%)
11	OH	**12**	82
13	NH_2	**14**	65
15	NPr^i_2	**16**	70

Scheme 4

Oxidation of limonene revealed that in certain cases steric factors govern regioselectivity in oxidations with TBHP catalyzed by $Rh_2(cap)_4$ (Scheme 5).[54] Thus, carvone was the major product of limonene oxidation despite the greater thermodynamic stability of allyl radical generated after hydrogen atom abstraction from the 3-position. Moreover, racemization of the stereocenter of limonene confirmed the formation of a symmetric allyl radical after hydrogen atom abstraction from the 6-position.

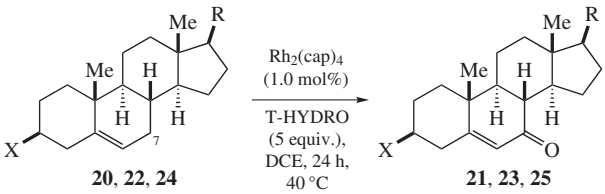
Steroidal substrates with a 5,6-double bond were selectively oxidized by TBHP in the presence of $Rh_2(cap)_4$.[54,55] These



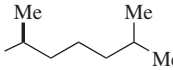
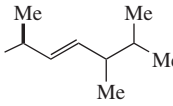
17 **18** **19**
44% racemic 7%

Scheme 5

oxyfunctionalizations occurred exclusively at the less hindered allyl position of the steroidal core (Scheme 6).[55] Acetylation of the hydroxyl group of cholesterol improved the yield of enone **23** (Scheme 6). Interestingly, the presence of unsaturation in the steroidal side chain of **24** did not interfere with the reaction, and oxidation furnishes enone **25** in 43% yield (Scheme 6). Furthermore, the dirhodium catalyzed allylic oxidation was easily scaled up to an 8 gram scale.[56]

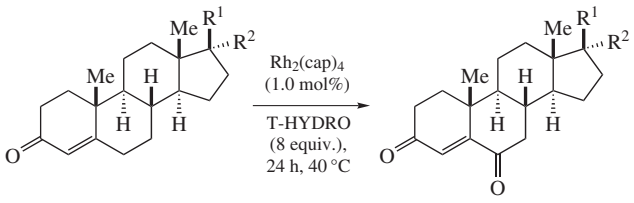


20, **22**, **24** **21**, **23**, **25**

Substrate	R	X	Product	Yield (%)
20		OH	**21**	63
22		OAc	**23**	80
24		OH	**25**	43

Scheme 6

Evaluation of solvent effects on allylic oxidation with T-HYDRO catalyzed by $Rh_2(cap)_4$ revealed that the presence of heterogeneous water improved the yield of enedione **27** from 50% in DCE to 68% (Scheme 7).[54] However, this effect was not general, and water had a detrimental effect on the oxidation of **28**.

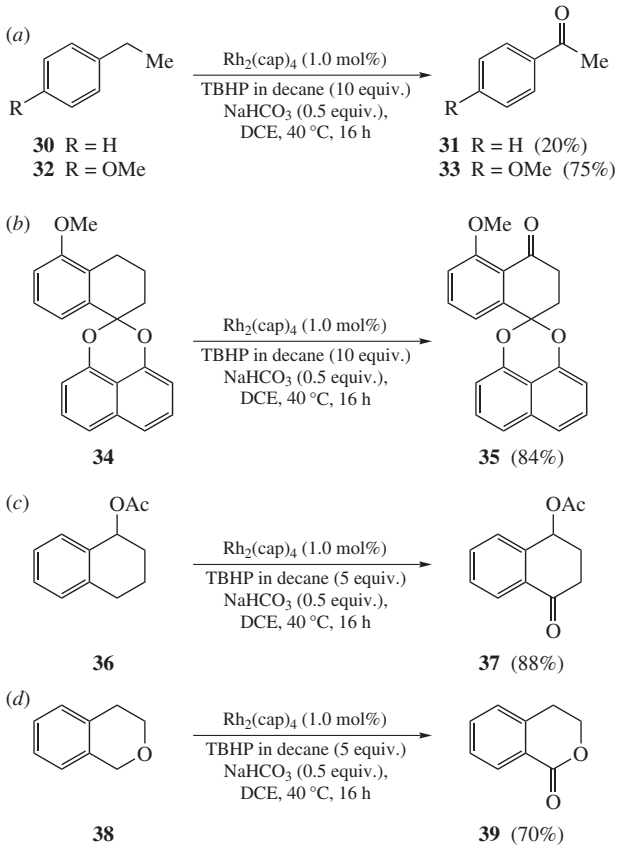


26, **28** **27**, **29**

Substrate	R^1	R^2	Solvent	Product	Yield (%)
26	OAc	H	DCE	**27**	50
			Water		68
28	=O		DCE	**29**	80
			Water		62

Scheme 7

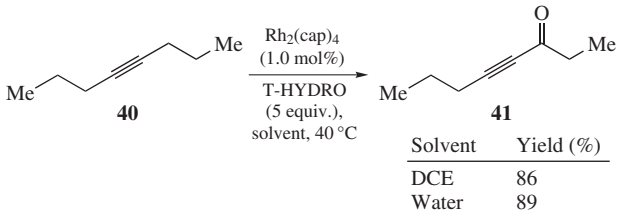
Oxidations of benzylic positions with the $Rh_2(cap)_4$ oxidative system are more challenging than allylic oxidations, and the presence of electron donating substituents in the aromatic ring enhances the rate of oxidation [Scheme 8(*a*)].[57] Benzylic oxidation provides a convenient synthesis of a precursor of palmaumycin CP_2 **35** [Scheme 8(*b*)]. Similar to the trends observed for allylic oxidation, steric factors direct the oxidation to the less substituted



Scheme 8

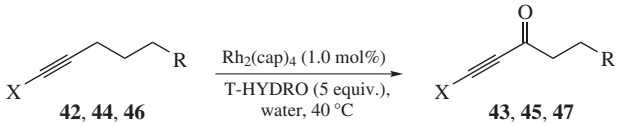
benzylic carbon [Scheme 8(*c*)], and electronic factors favor oxidation at the position adjacent to an electron donating atom such oxygen [Scheme 8(*d*)].

Alkynes readily undergo oxidation by TBHP catalyzed by $Rh_2(cap)_4$ affording ynones in 39–89% yield.[58] Oxidations of internal alkynes (Scheme 9) occur with higher yield than do terminal alkynes (Scheme 10). However, silylation of a terminal alkyne improves the yield of terminal ynone from 43 to 77%. Noteworthy, the dirhodium–T-HYDRO oxidative system achieves a 79% yield with an alkyne bearing a carboxylic acid group.



Solvent	Yield (%)
DCE	86
Water	89

Scheme 9

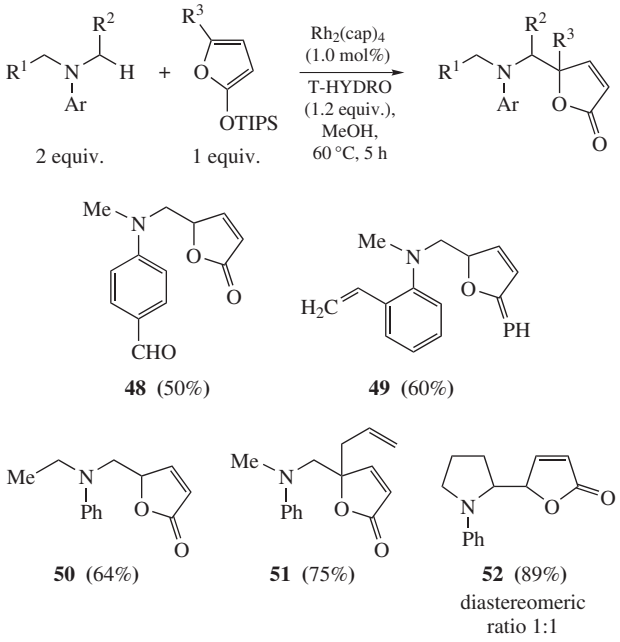


Substrate	X	R	Product	Yield (%)
42	H	Pr	**43**	43
44	TMS	heptyl	**45**	77
46	TMS	CO_2H	**47**	79

Scheme 10

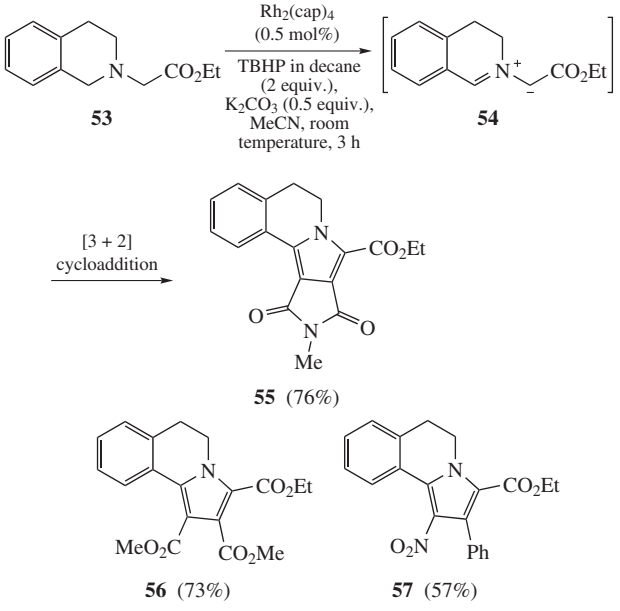
Transformations of amines and hydroxylamines

The oxidative Mannich reaction of *N*,*N*-dialkylanilines is one of the most synthetically useful protocols developed with the dirhodium caprolactamate–TBHP oxidative system.[11,59] The scope of *N*,*N*-dialkylanilines includes electron-rich as well as electron-poor *N*,*N*-dialkylanilines. Functionalization of carbon adjacent to nitrogen can be carried out in the presence of an aldehyde,[59] a labile functional group under other radical oxidative conditions[1,80] (Scheme 11). An *ortho*-vinyl substituent on the aromatic ring does not interfere with the reaction as well. This protocol allows the formation of C–C bonds between two secondary carbons as well as between tertiary and primary carbons, albeit without diastereocontrol (Scheme 11). Noteworthy, functionalization of nonsymmetrical *N*-ethyl-*N*-methylaniline occurs selectively at the methyl group.



Scheme 11

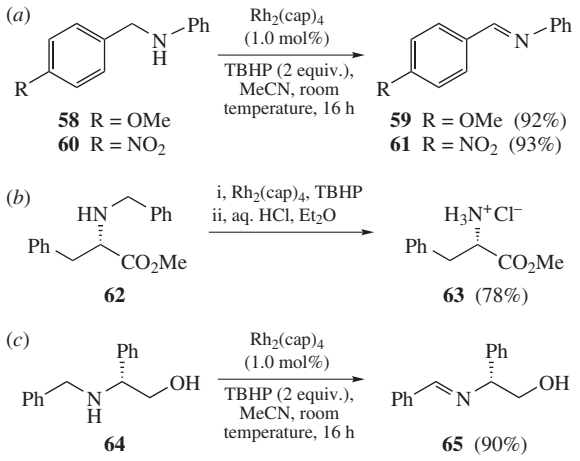
Lu developed a facile synthesis of a number of heterocyclic compounds from the more easily oxidized tetrahydroisoquinoline **53** (Scheme 12).[63] Anhydrous TBHP in the presence of $Rh_2(cap)_4$ converted **53** to an iminium ion that was subsequently deprotonated to furnish 1,3-dipole **54**. Addition of electron-poor alkenes or alkynes *via* syringe pump afforded [3 + 2]-cycloaddition products that, in the case of alkenes, were further oxidized



Scheme 12

under the reaction conditions to restore the aromaticity of the heterocyclic ring.

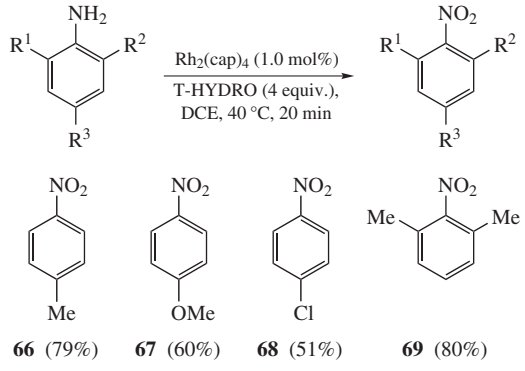
The dirhodium caprolactamate oxidative system selectively converts secondary amines to imines in 82–94% yields (Scheme 13).[60] *N*-Benzylanilines produce the corresponding imines in over 90% yields regardless of the electronic properties of the aromatic ring [Scheme 13(*a*)]. Thus, the developed protocol is general for benzyl group deprotection under mild oxidative conditions [Scheme 13(*b*)].



Scheme 13

The dirhodium catalyzed oxidative methodology also forms imines from aliphatic amines in 74–95% yields.[60] Acetonitrile is the solvent of choice for this transformation because this solvent outcompetes binding of deprotonated hydroperoxide to $Rh_2(cap)_4$ and decreases the rate of non-productive TBHP decomposition to molecular oxygen and di-*tert*-butyl peroxide. Similar to *N*,*N*-dialkylaniline oxidations, secondary amines are oxidized at the less substituted carbon adjacent to nitrogen [Scheme 13(*c*)].

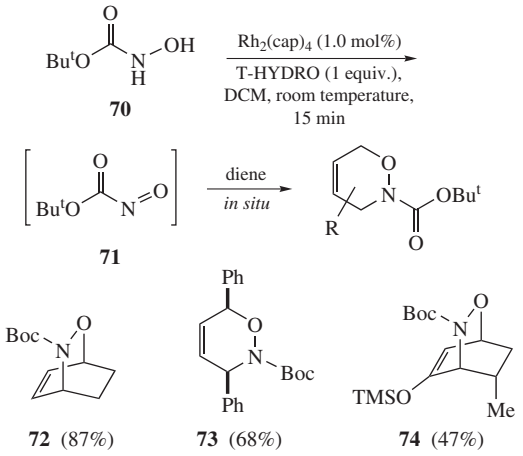
In the absence of substituents on the nitrogen atom, TBHP oxidizes the primary amino group of anilines to a nitro group in the presence of $Rh_2(cap)_4$ (Scheme 14).[34] Up to 80% yields were achieved with this methodology, and the scope of anilines includes those that are electron-rich and electron-poor. Substituents in the *ortho* position do not interfere with the reaction.



Scheme 14

Unlike an amino group in anilines, aliphatic primary amines form ketones upon treatment with TBHP in the presence of $Rh_2(cap)_4$.[34] In some instances oxidation occurs with C–C bond cleavage. The nature of this process and the criteria governing this selectivity are unclear.

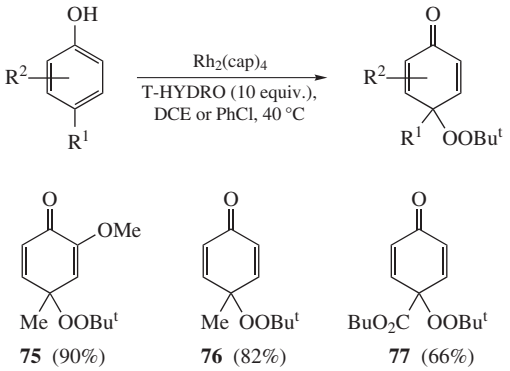
An amino group adjacent to the hydroxyl group is a convenient precursor to a nitroso group, as was elegantly shown by Lu in a cascade oxidation–Diels–Alder addition (Scheme 15).[62] According to this protocol, the Boc-functionalized hydroxyl amine **70** in the presence of dienes forms mono- and bicyclic skeletons in 47–87% yields under the mild oxidative conditions of the $Rh_2(cap)_4$–TBHP system. The resulting azoxy heterocycles are convenient precursors to *syn*-1,4-aminoalcohols.[62,81–84]



Scheme 15

Dearomatization

The dirhodium caprolactamate oxidative system has been applied to the oxidation of 4-substituted phenols[34,61] to furnish 4-peroxy-2,5-dienones in 57–99% yields (Scheme 16).[34] Substituents *ortho* to the hydroxyl group can vary in size and electronic properties and generally improve the yield of 2,5-dienones. Noteworthy, oxidation of electron-poor butyl paraben, an antifungal preservative in cosmetic products,[85,86] yielded dienone **77** in 66% yield (Scheme 16).



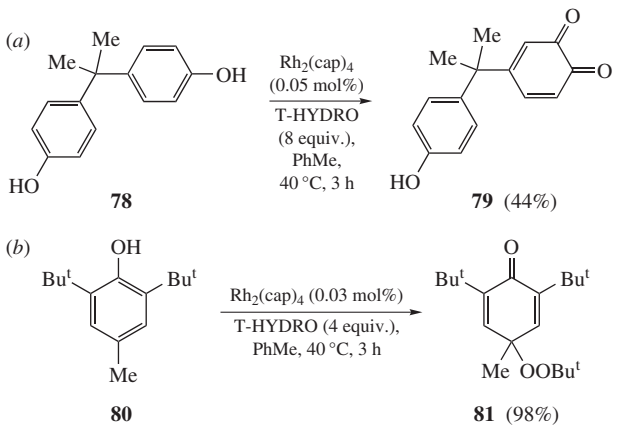
Scheme 16

A small amount of 2,4-dienones (*ortho*-quinones), products of *ortho* oxidation of phenols, were isolated in the $Rh_2(cap)_4$ catalyzed oxidation of phenols bearing isopropyl and *tert*-butyl groups at the 4-position.[34] Further increase in size of the 4-alkyl group (*e.g.*, bisphenol A **78**) makes *ortho* oxidation the dominant route [Scheme 17(*a*)].

Interestingly, conducting phenol oxidations in aromatic solvents drastically increases the reaction rate and allows lower loading of $Rh_2(cap)_4$. Thus, in toluene the effective amount of $Rh_2(cap)_4$ could be lowered from 1.0 mol% to just 0.03 mol% [Scheme 17(*b*)]. The nature of this acceleration is unclear.

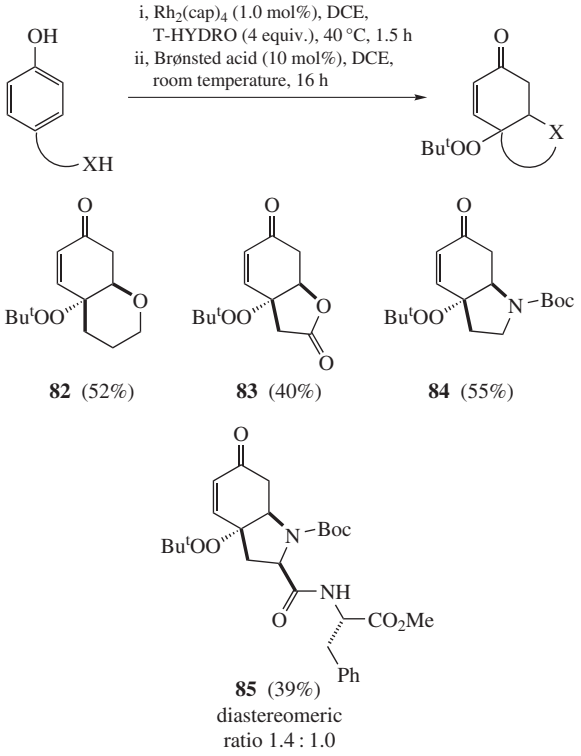
Phenol oxidation, like allylic oxidation, tolerates a variety of functional groups such as alcohol, carboxamidate, and carboxylic acid.[61] However, the presence of an electron-withdrawing group at the 4-position increases the amount of *ortho*-quinone product that decomposes under reaction conditions.

2,5-Dienones with tethered nucleophilic centers can be readily converted in a one-pot protocol to oxo- and aza-heterocycles in



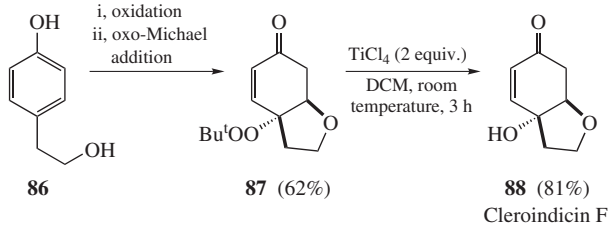
Scheme 17

39–62% yields by an addition of 10 mol% of a Brønsted acid (Scheme 18). The length of the tether can contain either two or three carbon atoms while possible nucleophiles include alcohol, carboxylic acid, and Boc-protected amine. Unfortunately, attempts to develop an asymmetric version of tandem phenol oxidation–Michael addition using BINOL-derived phosphoric acids achieved only 70% as the highest value of enantiomeric excess. Noteworthy, the $Rh_2(cap)_4$–TBHP catalytic system selectively oxidizes the phenol of the tyrosine residue in tyrosine–glycine and tyrosine–phenylalanine dipeptides. Subsequent aza-Michael addition furnishes heterocycle **85** that structurally resembles hexahydroindole.



Scheme 18

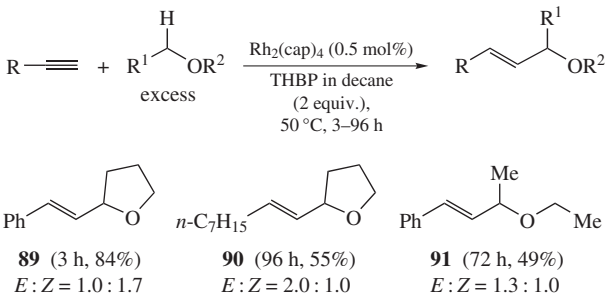
The synthetic utility of $Rh_2(cap)_4$ catalyzed phenol oxidation–Brønsted acid catalyzed oxo-Michael addition has been shown in the efficient synthesis of cleroindicin F (**88**),[61] a potential treatment for malaria[87–91] (Scheme 19). The target molecule was synthesized in just three steps at 50% overall yield from commercially available phenol and is a superior route than the syntheses reported by You (3 steps, 22% overall yield),[92] Pettus (10 steps, 18% overall yield),[87] and Hoveyda (9 steps, 17% overall yield).[93] Surprisingly, magnesium, zinc, and thiourea did not cleave O–O bond of cleroindicin F peroxide precursor. Only treatment of the peroxide with $TiCl_4$ afforded the desired transformation.



Scheme 19

C–C bond formation

Recently, Lu showed that the synthetic utility of $Rh_2(cap)_4$–TBHP catalytic system extends to C–C bond forming reactions.[94] Thus, α-oxo-radicals formed from ethers upon treatment with TBHP in the presence of dirhodium caprolactamate readily add across a single π-bond of terminal alkynes in 42–86% yield in an anti-Markovnikov fashion (Scheme 20). Both electron-rich and electron-poor aromatic alkynes are functionalized with ethers in just three hours, albeit with no control over diastereoselectivity. Aliphatic alkynes, on the other hand, require longer reactions times (up to 96 h). The catalytic C–C bond formation can be achieved in the presence of lactams and non-protected and benzyl or TMS protected hydroxyl groups.



Scheme 20

Interestingly, the C–C bond methodology is also applicable to phenol functionalization.[94] However, reported yields and regioselectivities require further optimization before this protocol can become synthetically useful.

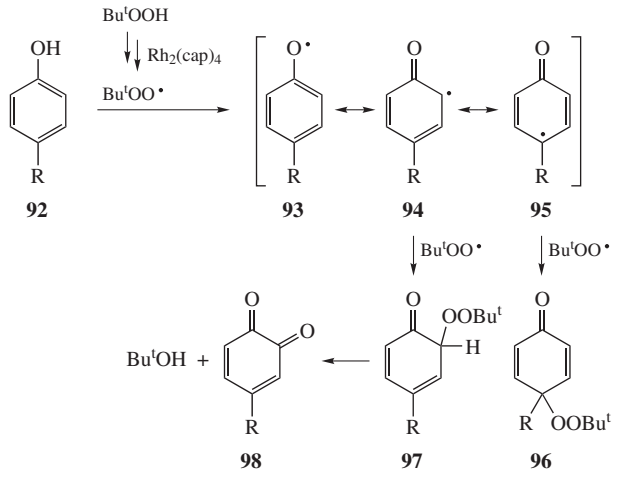
Mechanism

Dirhodium caprolactamate is a convenient catalyst for mechanistic investigations of oxidations with TBHP. Upon treatment with TBHP, $Rh_2(cap)_4$ forms its oxidized dirhodium(II,III) hydroxy complex[54,55] but not an oxo complex. The role of $Rh_2(cap)_4$ as a catalyst in converting TBHP into alkoxy and peroxy radicals has multiple precedents among other complexes with a one electron redox pair.[2] This section discusses our experimental evaluation of mechanistic models and comparative studies of $Rh_2(cap)_4$ with other catalysts employed in oxidations with TBHP.

The mechanism of phenol oxidations with TBHP catalyzed by $Rh_2(cap)_4$ unambiguously demonstrates the role of the dirhodium complex as a source of the *tert*-butylperoxy radical (Scheme 21). The dirhodium catalytic cycle starts with a one-electron reduction of TBHP that yields a *tert*-butoxy radical that, in turn, rapidly[95,96] abstracts hydrogen from hydroperoxide generating the more thermodynamically stable peroxy radical [Scheme 1, equations (1) and (2)]. A one-electron oxidation of TBHP by $Rh_2(cap)_4(OH)$ that forms $Rh_2(cap)_4$, water, and the *tert*-butylperoxy radical completes the catalyst turnover. In other words, $Rh_2(cap)_4$ generates a constant flux of peroxy radicals and is not directly involved in the phenol oxidation.

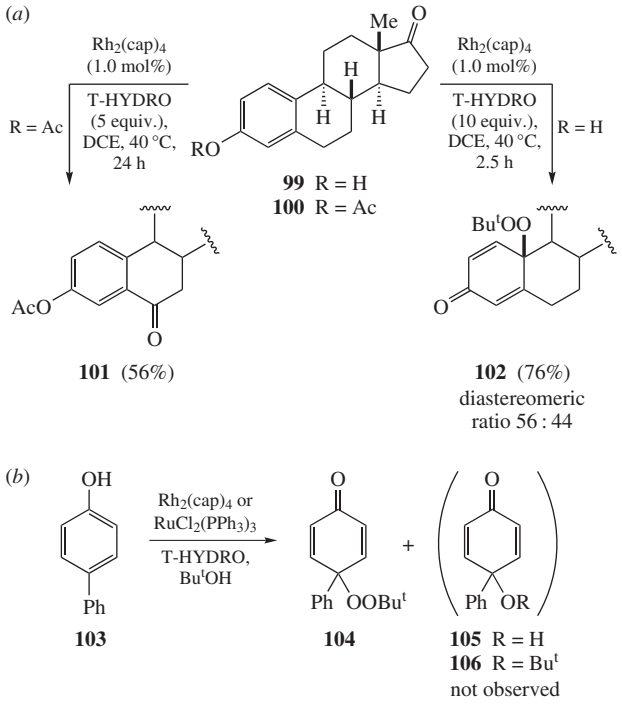
Experimentally, the presence of $Rh_2(cap)_4(OH)$ was identified by UV spectroscopy, and a non-zero concentration of the $Rh_2(cap)_4$ species was determined by HPLC in the course of $Rh_2(cap)_4$ catalyzed allylic oxidation.[54] The same conversion time for the $[Rh_2(cap)_4]^+BF_4^-$ catalyzed phenol oxidation confirmed that $[Rh_2(cap)_4]^+$ is the kinetically competent intermediate.[34]

The *tert*-butylperoxy radical, once formed, abstracts hydrogen from the hydroxyl group of phenol furnishing phenoxy radicals **93**–**95** (Scheme 21). Such radicals usually have a greater spin density at the 4-position (resonance form **95**) than at the 2-position (**94**). Thus, recombination of the phenoxy radicals with a *tert*-butylperoxy radical affords primarily 4-peroxy-2,5-dienones (**96**).



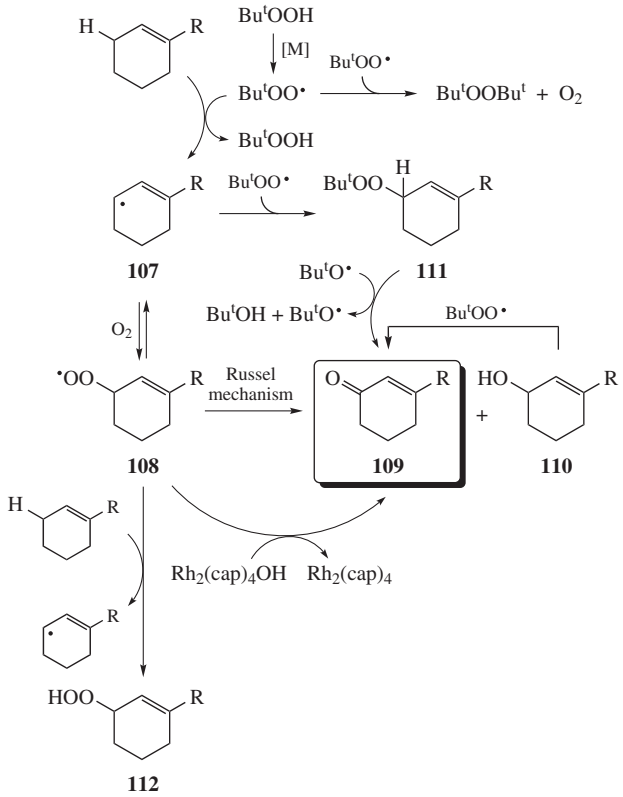
Scheme 21

The available experimental data support the proposed mechanism. First, benzylic oxidation becomes the dominant pathway if the hydroxyl group is capped with an acetyl group [Scheme 22(*a*)]. Second, $Rh_2(cap)_4$ and $RuCl_2(PPh_3)_3$ catalyzed phenol oxidation by TBHP in the presence of water or in *tert*-butyl alcohol yields no alcohol **105** or ether products **106** [Scheme 22(*b*)], which is consistent with a radical intermediate **93**–**95** and does not support a phenol cation intermediate proposed by Murahashi.[97]



Scheme 22

The mechanism of allylic oxidation involves hydrogen abstraction from carbon adjacent to the C–C double bond[98] by *tert*-butylperoxy radicals generated by $Rh_2(cap)_4$ (Scheme 23).[54] The resulting allyl radical **107** can react either with *tert*-butylperoxy radical[99,100] or with dissolved molecular oxygen.[101] A recombination of the *tert*-butylperoxy radical with the allyl radical forms a normally stable mixed peroxide **111** that can, however, be subsequently converted to enone **109** by a *tert*-butoxy radical.[54] On the other hand, reaction of the allyl radical with molecular oxygen forms an allylperoxy radical **108**. This pathway is dominant, presumably due to a higher concentration of O_2 in the solution than *tert*-butylperoxy radical.[101] However, electron-withdrawing groups attached to allyl group shift the equilibrium from the peroxy radical to the original allyl radical and lead to recombination with the *tert*-butylperoxy radical.[102–106] An allylperoxy radical can disproportionate to enone **109** and allyl alcohol **110** *via* Russell mechanism,[107] but this is only a minor process in reactions catalyzed by $Rh_2(cap)_4$.[54,55] The $Rh_2(cap)_4(OH)$ oxidized species can directly oxidize peroxy radical to enone by an, as yet, unknown pathway. In addition, the allylperoxy radical can abstract a hydrogen atom from the allylic position of an unreacted alkene to form allyl hydroperoxide **112**.[108]

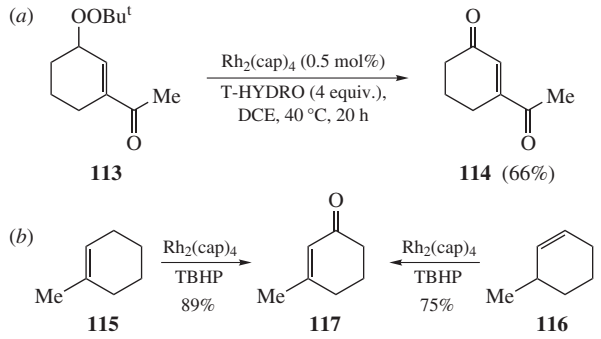


Scheme 23

A conversion of mixed peroxide **113** to the corresponding enone in 66% yield upon treatment with $Rh_2(cap)_4$ and T-HYDRO provides evidence supporting the proposed mechanism for allylic oxidation [Scheme 24(*a*)]. Moreover, oxidation of 1- (**115**) and 3-methylcyclohexene (**116**) converge to the most thermodynamically stable enone **117** [Scheme 24(*b*)].

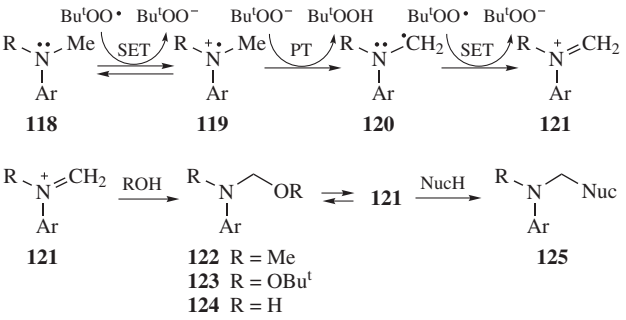
The oxidative Mannich reaction

The mechanism of oxidative Mannich reaction with TBHP has been studied in great detail. The oxidation of *N*,*N*-dialkylaniline consists of a slow reversible single electron transfer (SET) from *N*,*N*-dialkylaniline to the *tert*-butylperoxy radical followed by irreversible deprotonation of the cation radical **119** followed by rapid second single electron transfer (Scheme 25).[11] The



Scheme 24

resulting iminium ion **121** reacts initially with alcohol solvent forming alkoxy hemiaminal **122**, or with TBHP and water in the absence of nucleophilic solvent. Hemiaminal species **122**–**124** serve as a reservoir for the iminium ion **121** that is irreversibly trapped by the target nucleophile.



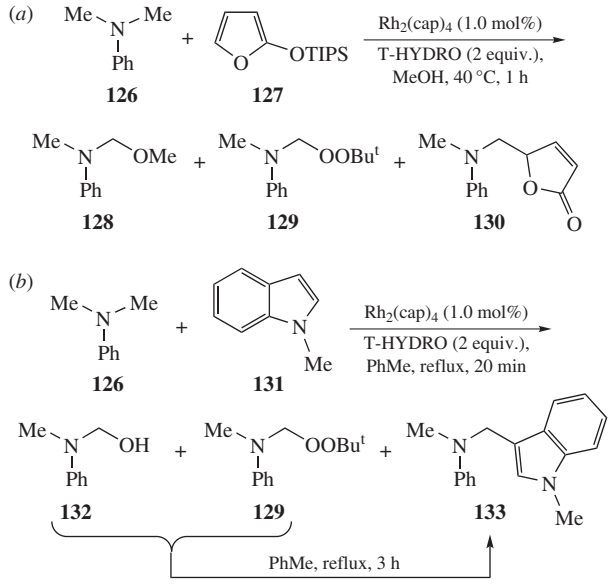
Scheme 25

Product and kinetic H–D isotope effects determined, respectively, for *N*-trideuteromethyl-*N*-methylanilines and 1:1 mixtures of *N*,*N*-dimethylanilines and *N*,*N*-bis(trideuteromethyl)anilines suggest competition between reverse SET and irreversible C–H bond cleavage.[11] A similar kinetic model was validated for *N*,*N*-dialkylaniline oxidations by cytochrome P450.[109] Oxidations of three *N*,*N*-dimethylanilines with T-HYDRO in methanol catalyzed by $RuCl_3$ and CuBr yielded product and kinetic isotope effects values that were identical within experimental error to values determined with $Rh_2(cap)_4$.[11] Hence, the *tert*-butylperoxy radical is a general oxidant of *N*,*N*-dialkylanilines, and formation of oxo-metal species[9,110–114] has no effect on the reaction. The same measurements done for $FeCl_3$- and $Co(OAc)_2$-catalyzed *N*,*N*-dialkylaniline oxidations with TBHP revealed a competition between pathways involving *tert*-butylperoxy radical and molecular oxygen.[11]

In the presence of siloxyfuran **127**, the $Rh_2(cap)_4$-catalyzed *N*,*N*-dimethylaniline **126** oxidation initially forms methoxy-hemiaminal **128** as the dominant product [Scheme 26(*a*)]. At higher conversion, the concentration of methoxy hemiaminal **128** decreases, the concentration of C-adduct **130** increases, and the concentration of peroxy hemiaminal **129** remains low. Thus, siloxyfuran **127** outcompetes TBHP for the reaction with an iminium ion formed from methoxy hemiaminal **128**. The oxidative Mannich reaction conducted in the absence of a nucleophilic solvent revealed formation of intermediate hemiaminal **132** and peroxy hemiaminal **129** that, upon further heating, converge to C-adduct **133** with *N*-methylindole **131** [Scheme 26(*b*)].

Perspectives

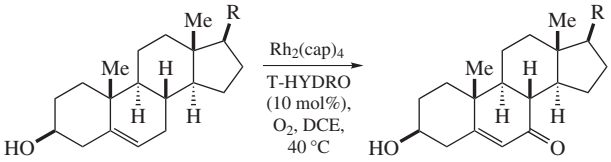
A detailed mechanistic understanding of $Rh_2(cap)_4$-catalyzed oxidations with TBHP enables further evolution of this area.



Scheme 26

Potential research directions include improvement of process parameters of existing transformations, investigation of the hydroperoxide structure–oxidation selectivity relationship, generalization of C–C bond cleavage reactions for which few examples currently exist,[34] development of novel reactions utilizing mixed peroxide functionality, and incorporation of $Rh_2(cap)_4$–TBHP oxidative protocols in cascade reactions and synthetic schemes.

Reduction of the need for an excess of TBHP in these oxidation reactions is one of the desirable improvements of process parameters. In the field of allylic oxidation, an increased concentration of molecular oxygen in solution *via* bubbling O_2 through the reaction mixture can improve allylic radical trapping that will reduce amount of mixed peroxide by-products and improve overall yield of allylic oxidations (Scheme 27). Furthermore, an external supply of O_2 might reduce excess of TBHP to sub-stoichiometric quantities and change the role of TBHP from a terminal oxidant to an initiator.



Scheme 27

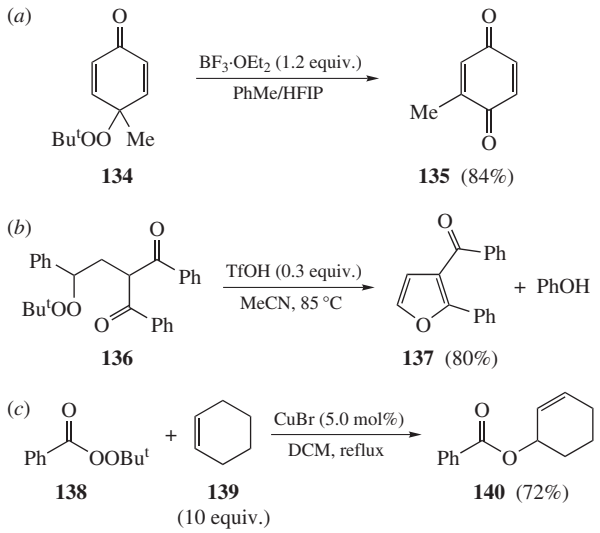
Several immobilization protocols developed for dirhodium complexes circumvent concerns associated with high cost of dirhodium catalysts.[115,116] However, a comprehensive evaluation is necessary for immobilized dirhodium complexes in oxidative reactions.

In all investigated $Rh_2(cap)_4$-catalyzed oxidations with TBHP, the *tert*-butylperoxy radical directly interacts with a substrate. Thus, structural changes within the hydroperoxide might uncover new selectivities. For example, commercially available and more sterically encumbered cumyl hydroperoxide might furnish selective *ortho* oxidation of phenols that can be trapped *in situ* by dienophiles.

Lu showed that α-oxo-radicals generated in the course of $Rh_2(cap)_4$-catalyzed oxidation can be intercepted by alkynes and phenols to form intermolecular C–C bonds (Scheme 20).[94] The mild oxidative conditions of $Rh_2(cap)_4$ catalyzed reactions with TBHP are compatible with a broad range of functional groups that is conducive for incorporation of this transformation in one-

pot cascade processes similar to phenol oxidation–Michael addition[61] and the hydroxylamine oxidation–Diels–Alder reaction.[62]

Transformations of mixed peroxides have received little attention, although some unique transformations have been uncovered (Scheme 28).[97,117–119] For example, Murahashi reported that treatment of 4-peroxy-2,5-dienone with $TiCl_4$[97] or BF_3[117] solution in toluene/1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) furnished 2-substituted *p*-quinones [Scheme 28(*a*)]. Similarly a strong Brønsted acid converts γ-peroxy ketone to furan in 80% yield [Scheme 28(*b*)].[118] Alternatively peroxy esters can also hydroacylate alkenes [Scheme 28(*c*)].[119]



Scheme 28

Conclusions

Dirhodium caprolactamate is a superior catalyst for oxidations with TBHP due to its ability to provide an optimal flux of *tert*-butylperoxy radicals that serve as mild one-electron oxidants or to abstract labile hydrogen atoms. The exceptional selectivity of oxidations with TBHP is coupled with a large diversity of functional groups that undergo functionalization under these conditions. The list of a few notable substrates include complex unsaturated steroids, *N*,*N*-dialkylaniline bearing a labile aldehyde group, and tyrosine oxidation in dipeptide structures. To date, the $Rh_2(cap)_4$–TBHP system has provided multiple synthetically-valuable transformations and continues to be a source for fruitful discoveries. Recent mechanistic investigations of the $Rh_2(cap)_4$-catalyzed Mannich reaction of *N*,*N*-dialkylanilines led to the discovery of an $FeCl_3$-catalyzed *N*,*N*-dialkylaniline oxidation by O_2.[10,11] Finally, a detailed mechanistic understanding of the developed processes serves as a reliable foundation for formulation of future research directions.

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