DOI: 10.1002/chem.201003060

A Mild Oxidative Aryl Radical Addition into Alkenes by Aerobic Oxidation of Arylhydrazines

Tsuyoshi Taniguchi,* Hisaaki Zaimoku, and Hiroyuki Ishibashi[a]

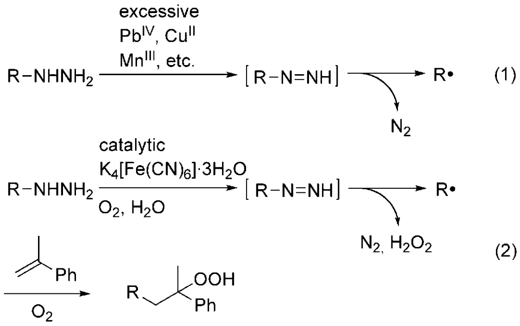
Abstract: A mild and practical oxyarylation of alkenes by oxidative radical addition has been developed by using aerobic oxidation of hydrazine compounds. The use of a catalytic amount of potassium ferrocyanide trihydrate ($K_4[Fe(CN)_6]\cdot 3H_2O$) and water accelerated this radical reaction to give peroxides or alcohols from simple alkenes in good yields. The environmentally friendly and economical radical reactions were achieved at room temperature in the presence of iron catalyst, oxygen gas, and water. A method involving aniline as a radical precursor is also described.

Keywords: iron • oxygen • peroxides • radical reactions • water

Introduction

Radical reactions have been used as powerful tools for C–C bond formation in synthetic chemistry.[1] As well as classical tin-mediated radical reactions, many useful radical reactions based on new concepts have recently been reported.[2]

Hydrazines have been reported to generate radical species by treatment with an oxidant, such as oxygen or metallic compounds, through the formation of diazenes (diimides) [Scheme 1, Eq. (1)].[3] Corey and Gross reported the formation of *tert*-butyl radicals by Pb^{IV}-mediated oxidation of *tert*-butylhydrazine and the reaction of the radical with nitroso compounds, providing a new preparation of *N*,*O*-di-*tert*-butyl hydroxylamines.[4] Asensio and co-workers have reported copper-mediated addition of an aryl radical formed from arylhydrazines to electron-withdrawing olefins.[5] Several examples of aryl–aryl coupling reactions that are performed in the presence of Pd^0, Hg^{II}, or Mn^{III} as an oxidant, have also been reported.[6] Myers and co-workers have reported the generation of an alkyl radical by treatment of alcohols with *p*-nitrobenzenesulfonylhydrazine under Mitsunobu conditions.[7] The addition of an aryl radical generated from diazonium salts to alkenes (Meerwein arylation) has also been reported.[8] However, many of these radical reactions still have some limitations, such as the use of an excess amount of toxic transition metals.



Scheme 1. Radical generation from hydrazine compounds.

Recently, iron has received attention as an inexpensive, less toxic substitute for rare metals such as palladium, and many efficient iron-catalyzed reactions such as C–C bond formation, have been developed.[9] Several iron-mediated radical reactions have also been reported.[10] Herein, we report an environmentally friendly potassium ferrocyanide trihydrate ($K_4[Fe(CN)_6]\cdot 3H_2O$) promoted aryl radical addition and subsequent aerobic oxidation of alkenes through the use of arylhydrazines in the presence of water [Scheme 1, Eq. (2)].[11–13]

Results and Discussion

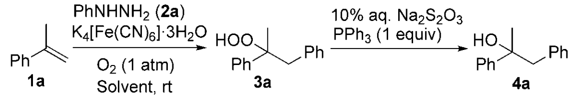
Treatment of a mixture of α-methylstyrene (**1a**) and phenylhydrazine (**2a**) (2.0 equiv) with oxygen gas[3a] in water for 33 h and subsequent reduction of the resultant peroxide **3a** by treatment of the reaction mixture with a 10% solution of $Na_2S_2O_3$ and PPh_3 (1 equiv), gave tertiary alcohol **4a** in 51% yield (Table 1, entry 1). When the reaction was carried out in the presence of a catalytic quantity (10 mol%) of potassium ferrocyanide(II) trihydrate, the reaction time was shortened (from 33 to 7.5 h) and the yield of **4a** was significantly improved (from 51 to 81%) (Table 1, entry 2). The reaction using potassium ferricyanide(III) ($K_3[Fe(CN)_6]$), as a catalyst afforded no improved yield compared to that

---

[a] Dr. T. Taniguchi, H. Zaimoku, Prof. Dr. H. Ishibashi
School of Pharmaceutical Sciences
Institute of Medical, Pharmaceutical
and Health Sciences
Kanazawa University
Kakuma-machi, Kanazawa 920-1192 (Japan)
Fax: (+81) 76-234-4439
E-mail: tsuyoshi@p.kanazawa-u.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201003060.

Table 1. Optimization of reaction conditions.

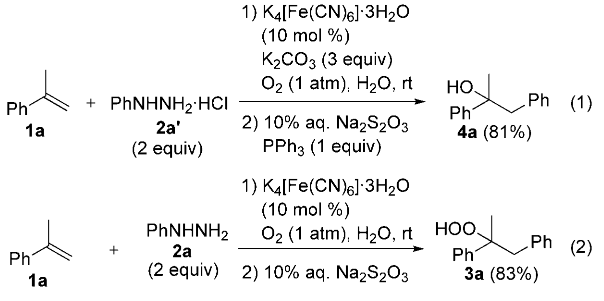


Entry	**2a** [equiv]	[Fe] (mol %)	Solvent	Time [h]	Yield [%][a]
1	2.0	none	H_2O	33	51
2	2.0	10	H_2O	7.5	81
3[b]	2.0	10	H_2O	6	71
4	2.0	10	DMF	8	48
5	2.0	10	MeOH	16	–
6	1.2	10	H_2O	8	63
7	3.0	10	H_2O	10	88
8	2.0	20	H_2O	11	82
9	2.0	5	H_2O	9.5	75
10[c]	2.0	10	H_2O	24	69

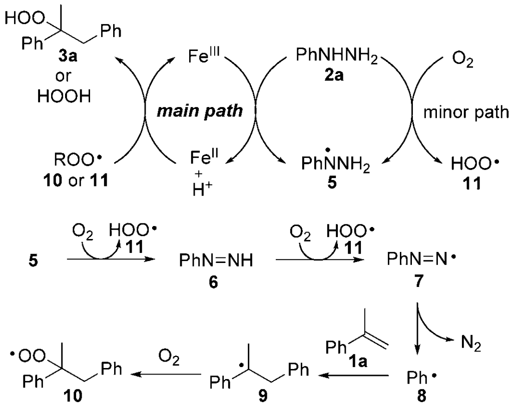
[a] Isolated yield of **4a**. [b] $K_3[Fe(CN)_6]$ was employed instead of $K_4[Fe(CN)_6]\cdot 3H_2O$. [c] Under air.

using ferrocyanide(II) (Table 1, entry 3). The use of *N*,*N*-dimethylformamide (DMF) instead of water as a solvent gave an unsatisfactory result (Table 1, entry 4), and the use of methanol caused decomposition of the substrate or product (Table 1, entry 5).[14] Decreasing or increasing the amount of **2a** resulted in only slight changes in yield (Table 1, entries 6 and 7). No significant change was observed by employing 20 mol % or 5 mol % iron catalyst (Table 1, entries 8 and 9). It was also found that a similar reaction using air instead of oxygen gas required prolonged reaction time (Table 1, entry 10).

When phenylhydrazine hydrochloride (**2a′**) was used as a radical precursor in the presence of K_2CO_3, a similar reaction took place to give alcohol **4a** in good yield [Scheme 2, Eq. (1)]. Peroxide product **3a** was readily isolated in good yield when PPh_3 was not present to reduce peroxide **3a** into alcohol **4a** [Scheme 2, Eq. (2)].[15]



Scheme 2. The reaction using phenylhydrazine hydrochloride salt **2a′** and isolation of peroxide **3a**.

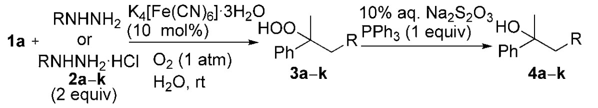


Scheme 3. Plausible mechanism of oxyarylation.

A plausible mechanism for the formation of hydroperoxide **3a** from α-methylstyrene (**1a**) by oxidation of phenylhydrazine (**2a**) is shown in Scheme 3. Although the present reaction proceeds slowly with only O_2 (Table 1, entry 1),[3] experimental results indicate that the addition of an iron catalyst that is a stronger oxidant than O_2 significantly accelerates this reaction (Table 1, entry 2).[16] Hence, it is reasonable that the iron catalyst accelerates the oxidation of phenylhydrazine (**2a**).[17] Because phenyldiazene (**6**) is known to be rapidly oxidized by O_2,[18] it is thought that the rate-determining step in the oxidation of phenylhydrazine is the first single-electron oxidation step. Therefore, single-electron transfer between phenylhydrazine (**2a**) and an iron catalyst would certainly take place to give phenylhydrazyl radical (**5**) in the initiating step.[19] Because radical species **5** would be expected to have high reactivity, radical **5** would be rapidly oxidized into phenyldiazene (**6**) by O_2.[19] As described above, phenyldiazene (**6**) is rapidly oxidized to the diazenyl radical **7** by O_2, and phenyl radical **8** is formed from radical **7** with release of molecular nitrogen.[18,19] Addition of phenyl radical **8** to α-methylstyrene (**1a**), followed by coupling of the resultant radical intermediate **9** with O_2 gives the peroxy radical **10**. Finally, redox reaction between hydrogen peroxide radical **11**, generated by the reduction of O_2 or peroxy radical **10**, and the Fe^{II} species, leads to the production of peroxide **3a** or hydroperoxide (H_2O_2) and regeneration of the Fe^{III} species.[20] Improvement in the yield of the product by using water as a solvent can be explained by the hydrophobic effect. The concentration of generated phenyl radical **8** and alkene **1a** by its hydrophobic nature in water might promote the radical addition reaction.[21]

Various hydrazines **2** were then subjected to the reaction with α-methylstyrene (**1a**). Arylhydrazines **2b–d**, bearing a halogen atom on the 4-position of the aromatic ring, gave products **4b–d** in good yields (Table 2, entries 2–4). The reaction of arylhydrazines **2e–g**, bearing an electron-donating group at either the 4- or 3-position of the aromatic ring, gave the corresponding alcohols **4e–g** in good yields (Table 2, entries 5–7), whereas 2-methylphenylhydazine (**2h**) gave a lower yield of product **4h** due to steric effects (Table 2, entry 8). Arylhydrazines **2i** and **2j**, bearing 4-trifluoro and 4-nitro groups on the aromatic ring, were insoluble in water and, hence, DMF was used as a solvent to give the desired products **4i** and **4j**, respectively (Table 2, entries 9 and 10).[22] The reaction of aliphatic hydrazine **2k** was found to be very sluggish (Table 2, entry 11).

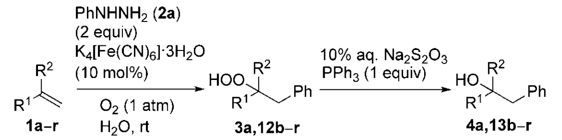
Table 2. Radical reactions of various hydrazines.

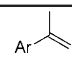
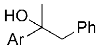
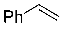
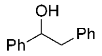
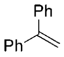
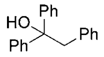
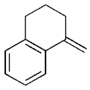
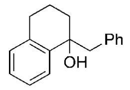
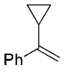
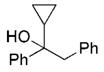
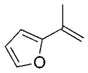
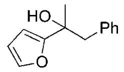
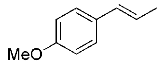
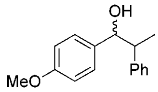
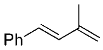
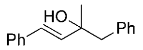
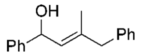
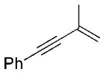
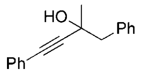
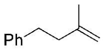
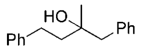
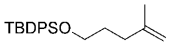
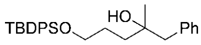
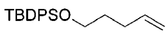
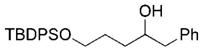
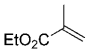
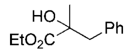
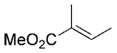
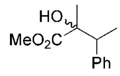
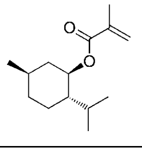
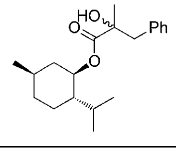


Entry	R		Time [h]	Yield [%][a]
1	Ph	**a**	7.5	81
2[b]	4-FC_6H_4	**b**	9	81
3[b]	4-ClC_6H_4	**c**	10	71
4[b]	4-BrC_6H_4	**d**	8	61
5[b]	4-$MeOC_6H_4$	**e**	4	74
6[b]	4-MeC_6H_4	**f**	9	71
7[b]	3-MeC_6H_4	**g**	14	70
8[b]	2-MeC_6H_4	**h**	6	47
9[c]	4-$CF_3C_6H_4$	**i**	20	59
10[c]	4-$NO_2C_6H_4$	**j**	11	70
11[b,d]	cyclohexyl	**k**	18	41

[a] Isolated yield of **4a–k**. [b] Hydrazine hydrochloride salt was used with K_2CO_3 (3 equiv). [c] DMF was used as solvent. [d] **2k** (4 equiv) was used at 50 °C.

Table 3. Radical reactions of various alkenes.



Entry	1		Time [h]	Product[a]	Yield [%]
					
1	Ar = C_6H_5	**1a**	7.5		81
2	Ar = 4-$MeOC_6H_4$	**1b**	9		80
3	Ar = 4-$NO_2C_6H_4$	**1c**	10		85
4	Ar = 4-BrC_6H_4	**1d**	11		78
5		**1e**	9		56
6		**1f**	7		82
7		**1g**	8		53
8		**1h**	11		75
9		**1i**	8		51
10		**1j**	9		37 (2:1)
11		**1k**	7	 	26 (**13k**) 25 (**13k′**)
12		**1l**	12		82
13[b]		**1m**	11		31
14[c]		**1n**	19		52
15[b]		**1o**	26		30
16		**1p**	6		63
17		**1q**	7		40 (2:1)
18		**1r**	8		66 (1:1)

[a] Yield of isolated product. [b] Compound **2a** (10 equiv) was used. TBDPS = *tert*-butyldiphenylsilyl.

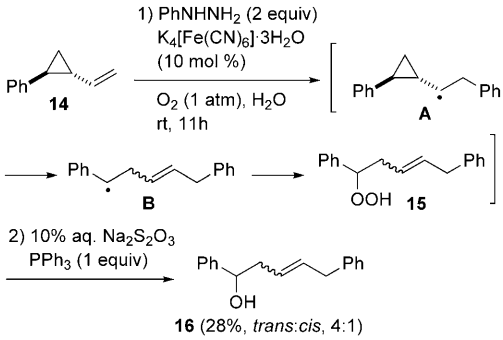
Reactions of various alkenes **1** with phenylhydrazine (**2a**) were then examined. α-Methylstyrene derivatives **1b–d**, bearing methoxy, nitro, and bromo groups on the aromatic ring, gave alcohols **13b–d** in good yields (Table 3, entries 2–4). The reaction of styrene (**1e**) gave secondary alcohol **13e**, although the yield was moderate (Table 3, entry 5). Other styrene-type alkenes **1f–j** also gave the corresponding tertiary alcohols **13f–j** in good to moderate yields (Table 3, entries 6–10). In the case of addition of the phenyl radical to **1h**, opening of the cyclopropane ring was not observed due to the stability of the resultant radical.[23] When diene **1k** was employed as a substrate, tertiary alcohol **13k** was obtained along with an equal amount of the regioisomer **13k′** (Table 3, entry 11). Reaction of enyne **1l** readily proceeded to give propargyl alcohol **13l** in good yield (Table 3, entry 12). Reactions of nonconjugated alkenes **1m–o** were sluggish and gave the corresponding alcohols **13m–o** in moderate yields (Table 3, entries 13–15). α,β-Unsaturated esters **1p** and **1q** also gave α-hydroxyesters **13p** and **13q**, respectively (Table 3, entries 16 and 17). In these cases, no Michael addition product with phenylhydrazine (**2a**) was detected. Unfortunately, the reaction of methacrylic ester **1r**, bearing a chiral auxiliary, showed no diastereoselectivity (Table 3, entry 18).[24]

When radical clock **14** was employed as a substrate, homoallyl alcohol **16** was obtained (Scheme 4). This strongly suggests that cyclopropylmetylene radical **A**, generated by addition of phenyl radical, undergoes a ring-opening reaction to give benzyl radical **B**, followed by trapping by O_2 to afford peroxide **15**.[23] Therefore, there is no doubt that the present reaction proceeds by a radical mechanism.

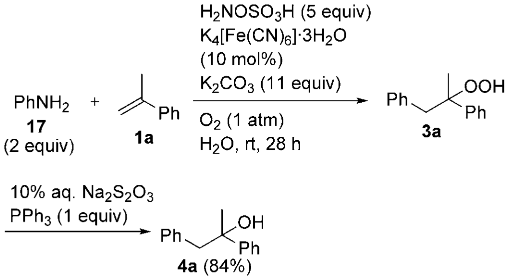
Finally, we found that the present reaction proceeded by formation of arylhydrazines in situ from aromatic amines with hydroxylamine-*O*-sulfonic acid. A mixture of **1a** and aniline (**17**) (2 equiv) was treated with hydroxylamine *O*-sulfonic acid (5 equiv) in water, in the presence of an iron catalyst and potassium carbonate, under an oxygen atmosphere, to give alcohol **4a** in good yield after reduction of the corresponding hydroperoxide **3a** with PPh_3 (Scheme 5).

Conclusion

We have developed the oxidative arylation of alkenes by oxygen-mediated formation of aryl radicals from arylhydra-



Scheme 4. Radical oxyarylation of **14**.



Scheme 5. The radical reaction using an aromatic amine as a precursor.

zines in the presence of a catalytic amount of $K_4[Fe(CN)_6]\cdot 3H_2O$ and water. Because the reaction involves the use of environmentally friendly and inexpensive reagents ($K_4[Fe(CN)_6]\cdot 3H_2O$, oxygen gas, and water), the present reaction provides a mild and economical method for the synthesis of peroxides and alcohols through new C–C bond formation. Further applications of the reaction in the presence of an iron catalyst are underway in our laboratory.

Experimental Section

General methods: All reagents were purchased commercially and used without further purification. IR spectra were recorded with a commercial FT/IR spectrometer (Shimadzu FTIR-8100). ^{1}H NMR spectra were recorded with 270, 500, or 600 MHz spectrometers (JEOL EX270 (270 MHz), JEOL JNM ECS400 (400 MHz) or JEOL JNM ECA600 (600 MHz)); chemical shifts (δ) are quoted relative to tetramethylsilane. ^{13}C NMR spectra were recorded at 67.5, 125, or 150 MHz with complete proton decoupling; chemical shifts (δ) are quoted relative to the residual signals of chloroform. Silica gel column chromatography was carried out on silica gel 60N. Mass spectra were recorded with a high-resolution mass spectrometer (JEOL JMS-SX-102A mass spectrometer) in fast atom bombardment modes (FAB).

Starting materials: Compounds **1a**, **1e**, **1f**, **1j**, **1p**, **1q**, **2a**–**k**, and **2a′** were commercially available. Compounds **1b**,[25] **1c**,[26] **1d**,[25] **1g**,[27] **1h**,[28] **1i**,[29]**1k**,[30] **1l**,[31]**1m**,[32] **1n**,[33] **1o**,[34] **1r**,[35] and **14**[36] were prepared according to literature methods.

General procedure for reactions using aryl hydrazines: Phenylhydrazine (104 mg, 1.0 mmol) was added to a mixture of alkene (0.50 mmol) and $K_4[Fe(CN)_6]\cdot 3H_2O$ (21.0 mg, 0.050 mmol) in water (5 mL), and the mixture was vigorously stirred at room temperature under an O_2 atmosphere (1 atm). After addition of 10% aqueous $Na_2S_2O_3$ (5 mL), PPh_3 (131 mg, 0.50 mmol) was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed successively with brine and dried with $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography (hexane/EtOAc) to give the desired product.

General procedure for reactions using aryl hydrazine hydrochloride salts: Phenylhydrazine hydrochloride (145 mg, 1.0 mmol) and K_2CO_3 (207 mg, 1.5 mmol) were added to a mixture of alkene (0.50 mmol) and $K_4[Fe(CN)_6]\cdot 3H_2O$ (21.0 mg, 0.050 mmol) in water (5 mL), and the mixture was vigorously stirred at room temperature under an O_2 atmosphere (1 atm). After addition of 10% aqueous $Na_2S_2O_3$ (5 mL), PPh_3 (131 mg, 0.50 mmol) was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed successively with brine and dried with $MgSO_4$. After removal of solvent under reduced pressure, the residue was purified by silica gel chromatography (hexane/EtOAc) to give the desired product.

Procedure for the reaction with aniline: Aniline (93.1 mg, 1.0 mmol), K_2CO_3 (760 mg, 5.5 mmol), and hydroxylamine *O*-sulfonic acid (283 mg, 2.5 mmol) were added to a mixture of **1a** (59.1 mg, 0.50 mmol) and $K_4[Fe(CN)_6]\cdot 3H_2O$ (21.0 mg, 0.050 mmol) in water (5 mL), and the mixture was vigorously stirred at room temperature under an O_2 atmosphere (1 atm) for 28 h. After addition of 10% aqueous $Na_2S_2O_3$ (5 mL), PPh_3 (131 mg, 0.50 mmol) was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed successively with brine and dried with $MgSO_4$. After removal of solvent under reduced pressure, the residue was purified by silica gel chromatography (hexane/EtOAc, 10:1) to give **4a** (88.9 mg, 84%).

Compound 4a: 81% yield; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.55$ (s, 3H), 1.87 (s, 1H), 3.01 (d, $J = 12.7$ Hz, 1H), 3.12 (d, $J = 12.7$ Hz, 1H), 6.97–6.99 (m, 2H), 7.17–7.25 (m, 4H), 7.30–7.33 (m, 2H), 7.37–7.40 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 29.4$, 50.5, 74.4, 125.0, 126.61, 126.62, 128.0, 130.6, 136.7, 147.6 ppm; IR ($CHCl_3$): $\tilde{\nu} = 3596$, 1603, 1497, 1447, 1221 cm^{-1}; HRMS (FAB): *m*/*z* calcd for $C_{15}H_{17}O$: 213.1280 $[M+H]^+$; found: 213.1286.

Compound 3a (from 1a without PPh$_3$): 83% yield; colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.57$ (s, 3H), 3.00 (d, $J = 15.5$ Hz, 1H), 3.16 (d, $J = 15.5$ Hz, 1H), 6.96–6.98 (m, 2H), 7.15–7.21 (m, 3H), 7.25–7.39 (m, 5H), 7.48 ppm (s, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 22.1$, 46.0, 86.5, 125.9, 126.4, 127.5, 127.7, 128.4, 130.7, 136.2, 143.5 ppm; IR ($CHCl_3$): $\tilde{\nu} = 3529$, 1603, 1497, 1448, 1331 cm^{-1}; HRMS (FAB): *m*/*z* calcd for $C_{15}H_{17}O_2$: 229.1229 $[M+H]^+$; found: 229.1230.

Compound 16: 28% yield (mixture of two isomers, *trans*/*cis*, 4:1); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$; major and minor isomers): $\delta = 2.10$ (br s, 2H; major and minor isomers), 2.44–2.52 (m, 2H; major isomers), 2.56–2.60 (m, 1H; minor isomer), 2.66–2.70 (m, 1H; minor isomer), 3.34 (d, $J = 7.2$ Hz, 2H; major isomer), 3.35 (d, $J = 7.2$ Hz, 2H; minor isomer), 4.70 (dd, $J = 7.2$, 6.0 Hz, 1H; major isomer), 4.74 (dd, $J = 7.4$, 5.4 Hz, 1H; minor isomer), 5.46–5.51 (m, 1H; major isomer), 5.52–5.56 (m, 1H; minor isomer), 5.67–5.74 (m, 2H; major and minor isomers), 7.09–7.37 ppm (m, 20H; major and minor isomers); ^{13}C NMR (150 MHz, $CDCl_3$; major and minor isomers): $\delta = 33.6$, 37.2, 39.0, 42.5, 73.6, 73.9, 125.7, 125.8, 125.9, 126.0, 127.1, 127.4, 127.6, 128.29, 128.35, 128.37, 128.42, 129.5, 129.6, 131.6, 133.1, 140.4, 140.6, 143.86, 143.9 ppm; IR ($CHCl_3$): $\tilde{\nu} = 3600$, 1601, 1495, 1452 cm^{-1}; HRMS (FAB): *m*/*z* calcd for $C_{17}H_{19}O$: 239.1436 $[M+H]^+$; found: 239.1440.

Acknowledgements

This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

---

[1] For reviews, see: a) *Radicals in Organic Synthesis* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**; b) *Topics in Current*

Chemistry Vols. 263 and 264: Radicals in Synthesis I and II (Ed.: A. Gansäuer), Springer, Berlin, **2006**.

[2] For recent examples, see: a) A. Gansäuer, C.-A. Fan, F. Piestert, *J. Am. Chem. Soc.* **2008**, *130*, 6916; b) J. Guin, R. Fröhlich, A. Studer, *Angew. Chem.* **2008**, *120*, 791; *Angew. Chem. Int. Ed.* **2008**, *47*, 779; c) S.-H. Ueng, M. MakhloufBrahmi, E. Derat, L. Fensterbank, E. Lacôte, M. Malacria, D. P. Curran, *J. Am. Chem. Soc.* **2008**, *130*, 10082; d) B. Quiclet-Sire, S. Z. Zard, *Org. Lett.* **2008**, *10*, 3279; e) T. Akindele, K. Yamada, K. Tomioka, *Acc. Chem. Res.* **2009**, *42*, 345; f) A. Beauseigneur, C. Ericsson, P. Renaud, K. Schenk, *Org. Lett.* **2009**, *11*, 3778; g) J. W. Tucker, J. M. R. Narayanam, S. W. Krabbe, C. R. J. Stephenson, *Org. Lett.* **2010**, *12*, 368.

[3] a) F. D. Chattaway, *J. Chem. Soc. Trans.* **1907**, *91*, 1323; b) R. L. Hardie, R. H. Thomson, *J. Chem. Soc.* **1957**, 2512; c) F. L. Scott, J. A. Barry, *Tetrahedron Lett.* **1968**, *9*, 2461; d) E. S. Huyser, R. H. S. Wang, *J. Org. Chem.* **1968**, *33*, 3901; e) H. A. O. Hill, P. J. Thornalley, *FEBS Lett.* **1981**, *125*, 235.

[4] a) E. J. Corey, A. W. Gross, *J. Org. Chem.* **1985**, *50*, 5391; b) R. Braslau, L. C. Burrill II, L. K. Mahal, T. Wedeking, *Angew. Chem.* **1997**, *109*, 247; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 237; c) N. Naik, R. Braslau, *Tetrahedron* **1998**, *54*, 667; d) R. Braslau, N. Naik, H. Zipse, *J. Am. Chem. Soc.* **2000**, *122*, 8421; e) R. Braslau, L. C. Burrill, M. Siano, N. Naik, R. K. Howden, L. K. Mahal, *Macromolecules* **1997**, *30*, 6445; f) D. Benoit, V. Chaplinski, R. Braslau, C. J. Hawker, *J. Am. Chem. Soc.* **1999**, *121*, 3904; g) R. Braslau, M. O. Anderson, F. Rivera, A. Jimenez, T. Haddad, J. R. Axon, *Tetrahedron* **2002**, *58*, 5513; h) S. Bath, N. M. Laso, H. Lopwz-Ruiz, B. Quiclet-Sire, S. Z. Zard, *Chem. Commun.* **2003**, 204; i) B. Stefane, S. Polanc, *Synlett* **2008**, 1279.

[5] T. Varea, M. E. González-Núñez, J. Rodrigo-Chiner, G. Asensio, *Tetrahedron Lett.* **1989**, *30*, 4709.

[6] a) J. B. Aylward, *J. Chem. Soc. C* **1969**, 1663; b) R. Nakajima, M. Kinosada, T. Tamura, T. Hara, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1113; c) A. S. Demir, Ö. Reis, E. Özgül-Karaaslan, *J. Chem. Soc. Perkin Trans. 1* **2001**, 3042; d) A. S. Demir, Ö. Reis, M. Emrullahoğlu, *Tetrahedron* **2002**, *58*, 8055. Recently, Wang and co-workers reported arylation of [60]Fullerene using arylhydrazines and oxidant, see: e) Z.-X. Chen, G.-W. Wang, *J. Org. Chem.* **2005**, *70*, 2380; f) G.-W. Wang, Y.-M. Lu, Z.-X. Chen, *Org. Lett.* **2009**, *11*, 1507.

[7] a) A. G. Myers, M. Movassaghi, B. Zheng, *J. Am. Chem. Soc.* **1997**, *119*, 8572; b) A. G. Myers, M. Movasssaghi, B. Zheng, *Tetrahedron* **1997**, *38*, 6569.

[8] For reviews on Meerwein arylation, see: a) J. A. Murphy in *Radicals in Organic Synthesis, Vol. 1* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**, pp. 298–315; b) M. R. Heinrich, *Chem. Eur. J.* **2009**, *15*, 820.

[9] For reviews, see: a) C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217; b) A. Fürstner, R. Martin, *Chem. Lett.* **2005**, *34*, 624; c) A. Correa, O. García Mancheño, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108; d) S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 3363; *Angew. Chem. Int. Ed.* **2008**, *47*, 3317; e) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500; f) A. Fürstner, *Angew. Chem.* **2009**, *121*, 1390; *Angew. Chem. Int. Ed.* **2009**, *48*, 1364; g) A. A. Sarhan, C. Bolm, *Chem. Soc. Rev.* **2009**, *38*, 2730.

[10] For examples of iron-mediated radical reactions, see: a) K. I. Booker-Milburn, D. F. Thompson, *J. Chem. Soc. Perkin Trans. 1* **1995**, 2315; b) U. Jahn, P. Hartmann, *Chem. Commun.* **1998**, 209; c) H. Danielec, J. Klügge, B. Schlummer, T. Bach, *Synthesis* **2006**, 551; d) Z. Li, L. Cao, C.-L. Li, *Angew. Chem.* **2007**, *119*, 6625; *Angew. Chem. Int. Ed.* **2007**, *46*, 6505; e) Y. Zhang, C.-J. Li, *Eur. J. Org. Chem.* **2007**, 4654; f) Z. Li, R. Yu, H. Li, *Angew. Chem.* **2008**, *120*, 7607; *Angew. Chem. Int. Ed.* **2008**, *47*, 7497; g) F. Vallée, J. J. Mousseau, A. B. Charette, *J. Am. Chem. Soc.* **2010**, *132*, 1514; h) N. Yoshikai, A. Mieczkowski, A. Matsumoto, L. Ilies, E. Nakamura, *J. Am. Chem. Soc.* **2010**, *132*, 5568; i) T. Taniguchi, N. Goto, A. Nishibata, H. Ishibashi, *Org. Lett.* **2010**, *12*, 112; j) T. Taniguchi, H. Ishibashi, *Org. Lett.* **2010**, *12*, 124; k) T. Taniguchi, Y. Sugiura, H. Zaimoku, H. Ishibashi, *Angew. Chem.* **2010**, *122*, 10352; *Angew. Chem. Int. Ed.* **2010**, *49*, 10154.

[11] For the synthesis of alcohols by addition of an α-hydroxyl carbon radical to α,β-unsaturated esters in the presence of O_2, see: a) T. Iwahama, S. Sakaguchi, Y. Ishii, *Chem. Commun.* **2000**, 613; b) K. Hirano, T. Iwahama, S. Sakaguchi, Y. Ishii, *Chem. Commun.* **2000**, 2457; c) T. Hara, S. Iwahama, Y. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2001**, *66*, 6425.

[12] For the synthesis of alcohols by air-assisted addition of Grignard reagents to alkenes, see: Y. Nobe, K. Arayama, H. Urabe, *J. Am. Chem. Soc.* **2005**, *127*, 18006.

[13] For the recent examples of oxyarylation, see: a) M. R. Heinrich, M. D. Kirschstein, *Tetrahedron Lett.* **2006**, *47*, 2115; b) M. R. Heinrich, A. Wetzel, M. Kirschstein, *Org. Lett.* **2007**, *9*, 3833; c) S. Kirchberg, R. Fröhlich, A. Studer, *Angew. Chem.* **2009**, *121*, 4299; *Angew. Chem. Int. Ed.* **2009**, *48*, 4235; d) A. D. Melhado, W. E. Brenzovich, Jr., A. D. Lackner, F. D. Toste, *J. Am. Chem. Soc.* **2010**, *132*, 8885; e) T. Kobatake, D. Fujino, S. Yoshida, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2010**, *132*, 11838; f) A. Dickschat, A. Studer, *Org. Lett.* **2010**, *12*, 3972.

[14] Under these conditions, acetophenone and benzyl alcohol were isolated. It was assumed that these compounds were produced by a 1,2-alkyl shift onto the oxygen atom of hydroperoxide **3a**.

[15] Mukaiyama and co-workers have reported cobalt-catalyzed hydroperoxidation of alkenes, see: a) T. Mukaiyama, T. Yamada, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 17. For recent examples of the synthesis of peroxide compounds, see: b) A. Natarajan, L. S. Kaanumalle, S. Jockusch, C. L. D. Gibb, B. C. Gibb, N. J. Turro, V. Ramamurthy, *J. Am. Chem. Soc.* **2007**, *129*, 4132; c) A. G. Griesbeck, D. Blunk, T. T. El-Idreesy, A. Raabe, *Angew. Chem.* **2007**, *119*, 9040; *Angew. Chem. Int. Ed.* **2007**, *46*, 8883; d) P. Ghorai, P. H. Dussault, *Org. Lett.* **2008**, *10*, 4577; e) Y. Li, H.-D. Hao, Q. Zhang, Y. Wu, *Org. Lett.* **2009**, *11*, 1615; f) P. Goswami, B. Das, *Tetrahedron* **2009**, *50*, 2384; g) L. S. Shul'pina, M. V. Kirillova, A. J. L. Pombeiro, G. B. Shul'pin, *Tetrahedron* **2009**, *65*, 2424; h) R. S. Murthy, M. Bio, Y. You, *Tetrahedron Lett.* **2009**, *50*, 1041.

[16] It is widely known that the reduction potential of O_2 to give $HOO^{\cdot}$ (hydroperoxy radical) is negative ($E = -0.13$ V), whereas the reduction potential of ferricyanide ($[Fe(CN)_6]^{3-}$) to give ferrocyanide ($[Fe(CN)_6]^{4-}$) is positive ($E = +0.36$ V).

[17] The oxidation of hydrazine compounds using a stoichiometric amount of $K_3[Fe(CN)_6]$ to give diazene compounds has been reported, see: a) S. Mannen, H. A. Itano, *Tetrahedron* **1973**, *29*, 3497; b) G. L. Carroll, A. K. Allan, M. K. Schwaebe, R. D. Little, *Org. Lett.* **2000**, *2*, 2531; c) Y. S. Park, S. C. Wang, D. J. Tantillo, R. D. Little, *J. Org. Chem.* **2007**, *72*, 4351.

[18] For the oxidation of phenyldiazene, see: a) P. C. Huang, E. M. Kosower, *J. Am. Chem. Soc.* **1968**, *90*, 2367; b) E. M. Kosower, P. C. Huang, T. Tsuji, *J. Am. Chem. Soc.* **1969**, *91*, 2325.

[19] Oxyhemoglobin-catalyzed aerobic oxidation of phenylhydrazine has been reported. In this reaction, it is presumed that oxyhemoglobin, which is an iron–oxygen complex, accelerates the first single-electron oxidation of phenylhydrazine, see: a) H. P. Misra, I. Fridovich, *Biochemistry* **1976**, *15*, 681; b) H. A. O. Hill, P. J. Thornalley, *Can. J. Chem.* **1982**, *60*, 1528.

[20] Oxidation of ferrocyanide to ferricyanide by peroxy radical has been reported, see: G. I. Khaikin, Z. B. Alfassi, R. E. Huie, P. Nera, *J. Phys. Chem.* **1996**, *100*, 7072.

[21] For examples of the significant effects of water as a solvent, see: a) H. Yorimitsu, T. Nakamura, H. Shinokubo, K. Oshima, K. Omoto, H. Fujimoto, *J. Am. Chem. Soc.* **2000**, *122*, 11041; b) S. Narayan, J. Muldoon, M. G. Finn, V. V. Fokin, H. C. Kolb, K. B. Sharpless, *Angew. Chem.* **2005**, *117*, 3339; *Angew. Chem. Int. Ed.* **2005**, *44*, 3275; c) I. Vilotijevic, T. F. Jamison, *Science* **2007**, *317*, 1189; The difference between homogeneous "in water" and heterogeneous "in the presence of water" has been discussed, see: d) A. P. Brogan, T. J. Dickerson, K. D. Janda, *Angew. Chem.* **2006**, *118*, 8278; *Angew. Chem. Int. Ed.* **2006**, *45*, 8100; e) Y. Hayashi, *Angew. Chem.* **2006**, *118*, 8281; *Angew. Chem. Int. Ed.* **2006**, *45*, 8103. An objection

against exaggerated claims for some advantages in using water has also been suggested, see: f) D. G. Blackmond, A. Armstrong, V. Coombe, A. Wells, *Angew. Chem.* **2007**, *119*, 3872; *Angew. Chem. Int. Ed.* **2007**, *46*, 3798.

[22] Although the effect of the substituent groups of arylhydrazines is unclear in the present reaction, it is known that the oxidation potential increases with the electron deficiency of an aromatic ring, see: a) Y. Zhao, F. G. Bordwell, J.-P. Cheng, D. Wang, *J. Am. Chem. Soc.* **1997**, *119*, 9125; b) G. Valverde-Aguilar, X. Wang, E. Plummer, J. V. Lockard, J. I. Zink, Y. Luo, M. N. Weaver, S. F. Nelsen, *J. Phys. Chem. A* **2008**, *112*, 7332.

[23] For radical clocks, see: M. Newcomb in *Radicals in Organic Synthesis, Vol. 2* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**, pp. 317–336. In the reversible ring opening–closing process of a cyclopropylmethyl radical, an α-cyclopropylbenzyl radical such as a radical generated from compound **1h** is thermodynamically favored. On the other hand, a 2-phenylcyclopropylmethyl radical, such as radical **A**, rapidly undergoes a ring-opening reaction to give a thermodynamically stable benzyl radical such as radical **B**.

[24] For rare examples of stereoselective hydroxylation by molecular oxygen, see: a) D. Sano, K. Nagata, T. Itoh, *Org. Lett.* **2008**, *10*, 1593; b) H. Lubin, A. Tessier, G. Chaume, J. Pytkowicz, T. Brigaud, *Org. Lett.* **2010**, *12*, 1496.

[25] A. Fryszkowska, K. Fisher, J. M. Gardiner, G. M. Stephens, *J. Org. Chem.* **2008**, *73*, 4295.

[26] W. M. Sherrill, R. Kim, M. Rubin, *Tetrahedron* **2008**, *64*, 8610.

[27] C. R. Johnson, B. D. Tait, *J. Org. Chem.* **1987**, *52*, 281.

[28] G. A. Olah, V. P. Reddy, G. K. S. Prakash, *Synthesis* **1991**, 29.

[29] G. W. Gribble, D. J. Keavy, S. E. Branzt, W. J. Kelly, M. A. Pals, *Tetrahedron Lett.* **1988**, *29*, 6227.

[30] M. J. Fuchter, J.-N. Levy, *Org. Lett.* **2008**, *10*, 4919.

[31] T. Hatakeyama, Y. Yoshimoto, T. Gabriel, M. Nakamura, *Org. Lett.* **2008**, *10*, 5341.

[32] H. Lebel, D. Guay, V. Paquet, K. Huard, *Org. Lett.* **2004**, *6*, 3047.

[33] T. Suzuki, T. Oriyama, *Synlett* **2000**, 859.

[34] L. A. Dakin, N. F. Langille, J. S. Panek, *J. Org. Chem.* **2002**, *67*, 6812.

[35] V. Athawale, N. Manjrekar, M. J. Athawale, *J. Mol. Catal. B: Enzym.* **2001**, *16*, 169.

[36] J. S. Baik, N. H. Lee, *Bull. Korean Chem. Soc.* **2006**, *27*, 765.

Received: October 22, 2010

Please note: Minor changes have been made to this manuscript since its publication in *Chemistry–A European Journal* Early View. The Editor