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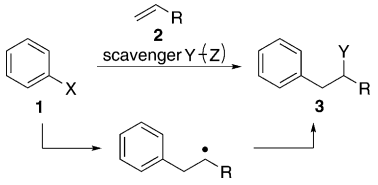
Synthesis

Manganese(IV)-Mediated Hydroperoxyarylation of Alkenes with Aryl Hydrazines and Dioxygen from Air

Stephanie Kindt, Hannelore Jasch, and Markus R. Heinrich*[a]

Abstract: We report a new carbooxygenation-type version of the Meerwein arylation in which the introduction of oxygen is achieved by using dioxygen from the air. In this way, hydroperoxides were obtained from activated as well as non-activated alkenes by oxidizing aryl hydrazines with manganese dioxide. The best results were obtained with α-substituted acrylates. Importantly, the aryl hydrazine has to be added slowly to the reaction mixture to allow sufficient uptake of dioxygen from the air. Competition and labeling experiments revealed hydroperoxyl radicals as novel oxygen-centered radical scavengers.

Through many recent developments, especially those in the field of photocatalysis,[1] the Meerwein arylation,[2] dating back to 1939, has become a highly versatile radical multicomponent reaction for the functionalization of alkenes (Scheme 1). Over the last few decades, new aryl radical sources such as bromo- and iodobenzenes (X = Br, I) have been reported in addition to the traditionally used diazonium salts **1** (X = N_2^+). Non-activated alkenes are now tolerated as well as the activated alkenes (e.g., acrylates, **2**, R = COOR′; styrene, **2**, R = Ph) originally preferred. In addition, a variety of novel radical scavengers has been discovered for the introduction of a broad range of functional groups or atoms, Y.[3]



Scheme 1. The Meerwein arylation.

Particularly useful are nitrogen- and oxygen-substituted arylation products **3** (Y = NR^1R^2, OR^1).[3a] Whereas early examples of carbooxygenations[4] with diazonium and copper(II) salts were limited to 1,3-butadienes,[5] a far broader range of activated and non-activated alkenes is tolerated in iron(II)-mediated reactions with TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] as a radical scavenger.[6] An improved metal-free version of this reaction has been reported by Studer and co-workers.[7,8] In addition to TEMPO, dioxygen has recently emerged as an oxygen-introducing "reagent" in Meerwein arylations. Examples of such reactions are ferrocyanide-catalyzed carbooxygenations by Taniguchi and co-workers,[9,10] manganese(III) acetate-mediated oxyarylations of alkenes with aryl boronic acids by Studer and Dickschat,[11] and carbohydroxylations with phenylazocarboxylates studied by our group.[12] Other than one single example with α-methylstyrene,[9] all of the dioxygen-based reactions reported so far rely on the presence of a pure oxygen atmosphere. In this communication, we report a simple carbooxygenation reaction with dioxygen from air.

To generate the required aryl radicals under oxidative reaction conditions, we used phenyl hydrazines in combination with the strong oxidant manganese dioxide, which was used in its commercially available form. Studies on aryl radical generation from aryl hydrazines with various oxidants have recently been reported by the research groups of Demir,[13] Taniguchi,[9] Chen,[14] and our group.[15] To optimize the reaction conditions, we started with an experiment in which the aryl hydrazine **4a** was added over 20 min to a stirred mixture of alkene **5a**, manganese dioxide, acetic acid, and acetonitrile in an open flask at room temperature (Table 1, entry 1). The desired hydroperoxide was first obtained in a low yield of 25%, but the observation that 4,4′-dichloroazobenzene was formed as the major product (43%) led us to increase the time over which **4a** was added. This modification successfully reduced the undesired homocoupling of **4a** (entry 2), which probably occurs through aryl radical addition onto the intermediate phenyldiazene (see structure **10**, Table 4).[16] Having recognized the remarkable dependence of the hydroperoxyarylation on the slow addition of aryl hydrazine **4a**, we kept the longer addition time of 1 h for all further experiments. Variations of the reaction temperature (Table 1, entries 3, 4) did not lead to any improvement. Acetic acid is expected to be beneficial for the activation of the oxidant manganese dioxide, and the concurrent deactivation of the hydrazine through partial protonation appears to play a minor role (Table 1, entry 5).[17] An attempt to accelerate the oxidation of aryl hydrazine **4a** by increasing the solubility of MnO_2 through the addition of water failed (Table 1, entry 6), as did two attempts to decrease the amount of MnO_2 through prior activation of the oxidant.[18] After a control experiment under an argon atmosphere had unambigu-

[a] S. Kindt, Dr. H. Jasch, Prof. Dr. M. R. Heinrich
Department für Chemie und Pharmazie, Pharmazeutische Chemie
Friedrich-Alexander-Universität Erlangen-Nürnberg
Schuhstrasse 19, 91052 Erlangen (Germany)
E-mail: markus.heinrich@fau.de

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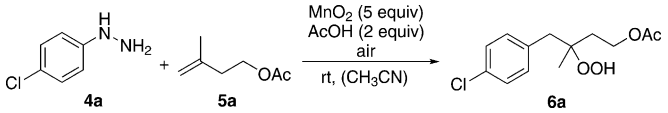
Table 1. Optimization experiments.



4a **5a** **6a**

Entry	Variation compared with standard conditions[a]	Yield [%][b]
1	–	25
2	**addition of 4a over 1 h**	**51**, **47**[c]
3	0 °C, 1 h[d]	3
4	40 °C, 1 h[d]	40
5	absence of acetic acid[d]	26
6	solvents: CH_3CN/H_2O (10:1)[d]	–
7	argon atmosphere[d]	–
8	stirring vigorously[d]	49
9	addition of KO_2 (1 equiv)[d]	54
10	addition of 2 equiv of **4a**[d]	32

[a] Standard conditions: **4a** (1.00 mmol in 4 mL CH_3CN, added over 20 min), **5a** (6.00 mmol), MnO_2 (5.00 mmol), acetic acid (2.00 mmol), CH_3CN (5 mL), rt. [b] Yield determined by addition of dimethyl terephthalate as an internal standard. [c] Yield after purification by column chromatography. [d] Addition of **4a** over 1 h.

ously proved the importance of dioxygen from air (Table 1, entry 7), we tried to improve the dioxygen saturation of the reaction mixture through vigorous stirring (Table 1, entry 8); however, this did not increase the yield. Slightly better yields were obtained with potassium superoxide as an additive (Table 1, entry 9), whereas a run with double the amount of aryl hydrazine (2 mmol) showed that the alkene and manganese dioxide should be used in excess of six and five equivalents, respectively.

As the improvement obtained by addition of potassium superoxide was not decisive (Table 1, entry 9), and as our main objective was to use dioxygen from air as the oxygen-centered scavenger, the optimized conditions (Table 1, entry 2) were employed to explore the scope and limitations of the hydroperoxyarylation reaction (Table 2).

Owing to the synthetic value of hydroperoxides in many transformations,[19] we combined our study with an investigation of the stability of the hydroperoxides with regard to purification by column chromatography. In earlier studies, the primarily obtained hydroperoxides could either not be isolated[11] or were reduced to the corresponding alcohols[9] prior to chromatography. From all the reactions with butenyl acetate **5a** (Table 2, entries 1–5), the desired hydroperoxides were obtained in moderate to good yields with volatile chlorobenzene as the only significant byproduct. Purification of **6a**–**e** by column chromatography on deactivated silica gel was possible without noticeable decomposition and the reliability of the yields determined by comparison with an internal standard could be verified in this way. Significantly lower yields were produced with 2-methallyl acetate (**5b**; Table 2, entries 6 and 7), probably owing to increased hydrogen abstraction from the allylic position of the alkene.[20] As shown by the spectra of the crude products, in which only **6f** and **6g** appeared, fragmentation to the corresponding ketones **7f** and **7g** (Table 3) does occur during purification on silica gel.[21] The acrylates **5c**–**e** almost always gave good to high yields of clean hydroperoxides before purification (Table 2, entries 8–10, 12–15). On silica gel, significant reduction of the hydroperoxides **6h**–**n** to the corresponding alcohols was observed. Reduction of **6i** occurred to a much lower extent (only 3%) when Al_2O_3 was used for purification. However, product separation from byproducts is likely to be more difficult with this sorbent. The hydroperoxide **6p**, obtained from aryl hydrazine **4a** and α-methylstyrene (**5f**) in moderate yield, remained stable during column chromatography (Table 2, entry 16), whereas the product of 2-methacrylonitrile (**5g**) gave **6q** in good yield, but clean and quantitative fragmentation was observed during purification (Table 3). Monosubstituted alkenes like acrylonitrile (**5h**) and methyl acrylate (**5i**) are less suited for hydroperoxyarylations owing to the formation of unstable products, such as cyanohydrins (Table 2, entry 18),[22] or competing alkene oligomerization (Table 2, entry 19). Accordingly, an experiment with only two equivalents of alkene **5i** gave a slightly improved yield of **6s** (34% vs. 29% with 6 equiv of **5i**).

Regarding the reduction of hydroperoxides to their corresponding alcohols, we found sodium thiosulfate to be particu-

Table 2. Hydroperoxyarylation—scope and limitations.[a]

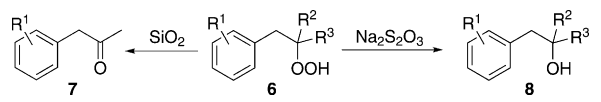
4a-f **5a-i** (6 equiv) **6a-s**

Entry	Aryl hydrazine **4** R^1=	Alkene **5** R^2=	R^3=	Product	Yield[b] [%]	Yield[c] [%]
1	4-Cl (**4a**)	$(CH_2)_2OAc$ (**5a**)	Me	**6a**	51	47
2	H (**4b**)	$(CH_2)_2OAc$ (**5a**)	Me	**6b**	58	55
3	4-F (**4c**)	$(CH_2)_2OAc$ (**5a**)	Me	**6c**	52	46
4	4-Br (**4d**)	$(CH_2)_2OAc$ (**5a**)	Me	**6d**	40	37
5	4-CN (**4e**)	$(CH_2)_2OAc$ (**5a**)	Me	**6e**	53	51
6	4-Cl (**4a**)	CH_2OAc (**5b**)	Me	**6f**	23	**7f**[d]
7	4-CN (**4e**)	CH_2OAc (**5b**)	Me	**6g**	37	**7g**[d]
8	4-Cl (**4a**)	CO_2Me (**5c**)	Me	**6h**	67	26 + 30[e]
9	H (**4b**)	CO_2Me (**5c**)	Me	**6i**	quant.	65 + 22[e]
10	4-CN (**4e**)	CO_2Me (**5c**)	Me	**6j**	75	67 + 5[e]
11	3-OMe (**4f**)	CO_2Me (**5c**)	Me	**6k**	41 + 6[e]	29 + 6[e]
12	4-Cl (**4a**)	CO_2Et (**5d**)	Me	**6l**	58	36 + 10[e]
13	H (**4b**)	CO_2Et (**5d**)	Me	**6m**	quant.	n.d.
14	4-CN (**4e**)	CO_2Et (**5d**)	Me	**6n**	74	47 + 22[e]
15	H (**4b**)	CO_2tBu (**5e**)	H	**6o**	55	n.d.
16	4-Cl (**4a**)	Ph (**5f**)	Me	**6p**	43	40
17	4-Cl (**4a**)	CN (**5g**)	Me	**6q**	70	**7f**[d]
18	4-Cl (**4a**)	CN (**5h**)	H	**6r**	19	10[e]
19	4-Cl (**4a**)	CO_2Me (**5i**)[f]	H	**6s**	34 + 7[e]	27 + 14[e]

[a] Standard conditions: **4a**–**f** (1.00 mmol in 4 mL CH_3CN, added over 1 h), **5a**–**i** (6.00 mmol), MnO_2 (5.00 mmol), acetic acid (2.00 mmol), CH_3CN (5 mL), rt. [b] Yield determined by addition of an internal standard. [c] Yield(s) after purification by column chromatography. [d] Hydroperoxides **6f**, **6g**, and **6q** underwent clean fragmentation to ketones **7f** and **7g** upon purification by column chromatography (see also Table 3). [e] Yield of corresponding alcohol. [f] Methyl acrylate (**5h**) (2.00 mmol).[27]

larly useful (Table 3).[23] In the case in which a labile cyanohydrin, **8q**, is obtained from a hydroperoxide such as **6q**, the pH value of the reaction mixture had to be controlled by a citrate buffer.[24] A possible explanation for the exceptionally high yields of the experiments with phenyl hydrazine (**4b**; Table 3, products **6i**, **6m**, **8i**, **8m**) could be that this was the only hydrazine that could be submitted to the reactions without prior treatment of its hydrochloride salt with aqueous sodium hydroxide and subsequent extraction.

Table 3. Transformation of hydroperoxides on silica gel and through reduction with sodium thiosulfate.



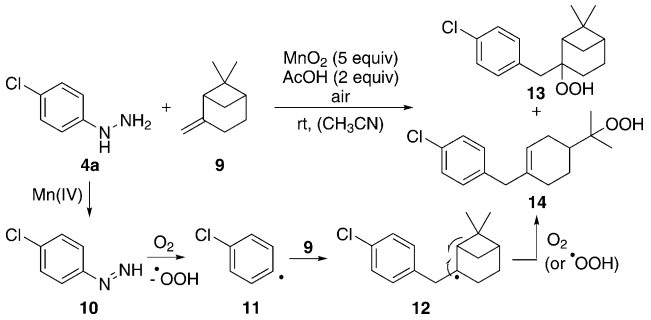
Entry	Ketone **7** [%][b]	Hydroperoxide **6** [% yield from **4** and **5**][a]	Alcohol **8** [% yield over 2 steps][b]
1	**7f** [quant.]	**6f** [23]	–
2	**7g** [quant.]	**6g** [37]	–
3		**6h** [70]	**8h** [55]
4		**6i** [quant.]	**8i** [91]
5		**6j** [67]	**8j** [54]
6		**6l** [41]	**8l** [39]
7		**6m** [quant.]	**8m** [quant.]
8		**6n** [58]	**8n** [46]
9		**6o** [55]	**8o** [55]
10	**7f** [quant.]	**6q** [70]	**8q** [63]
11		**6s** [34 + 7[c]]	**8s** [41]

[a] Yield determined by internal standard. [b] Yield after purification by column chromatography. [c] Yield of corresponding alcohol **8s**.

To get some initial insights into the factors that influence the trapping of the intermediate alkyl radicals by dioxygen or other related species, β-pinene (**9**) was employed as the alkene (Table 4). After aryl radical **11** is formed from diazene **10**,[16] the addition of **11** to **9** leads to alkyl radical **12**. Depending on the rate of trapping by the oxygen atom-centered radical scavenger, **12** will undergo ring opening to give **13** or **14** as the final product.[25] Under our standard conditions (see Table 2), a 4:3 ratio of ring-closed to ring-opened product **13**/**14** was found and, in accordance with the effect observed in the optimization study (Table 1, entry 1), trapping becomes less efficient when aryl hydrazine **4a** is added in only 15 min (Table 4, entry 2).

Taking into account the low solubility of dioxygen in air-equilibrated acetonitrile (2.42 mM),[26] this observation is not surprising, as the average volume of 7 mL of acetonitrile used in the experiments can only dissolve 0.017 mmol of dioxygen at a time. This value corresponds to 0.9% or 1.7% of the stoichiometrically required amount, depending on whether dioxygen is required for two or only one of the mechanistic steps (**10**→**11** and/or **12**→**13**/**14**). It therefore appears to be a crucial element for the success of such hydroxyperoxyarylation reactions that the reaction mixture is given enough time to equilibrate and replace used dioxygen by taking up more from the air. A control experiment under pure dioxygen gas led to the expected predominance of the ring-closed product **13** (Table 4, entry 3). Attempts to further accelerate the trapping of **12** by the addition of manganese(II) ions[27] did not lead to significant improvements (Table 4, entries 4, 5 cf. entries 1, 3). Remarkably improved ratios of **13**/**14** were, however, observed upon addition of increasing amounts of potassium superoxide (Table 4, entries 6–8), an observation that suggests that the hydroperoxyl radicals formed in step **10**→**11** might play an important role in the trapping of **12** to give **13** or **14**. Comparison of the experiments in entries 8 and 9 shows that sufficient acetic acid has to be present to maintain the beneficial effect of KO_2, probably by ensuring protonation of the superoxide ions to hydroperoxyl radicals. Unsurprisingly, the combination of superoxide and a dioxygen atmosphere led to hydroperoxide **13** without detectable amounts of **14** (Table 4, entry 10).

Table 4. Competition experiments.



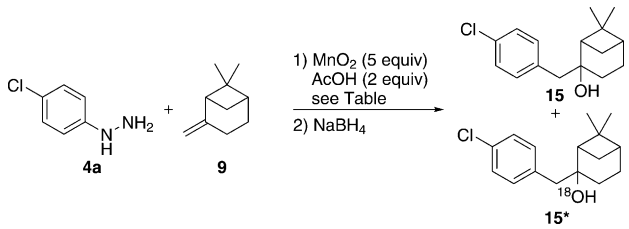
Entry	Variation compared with standard conditions[a]	Ratio **13**:**14**[c]
1	–	4:3
2	addition of **4a** over 15 min	1:2
3	under O_2 atmosphere	5:1
4	addition of $MnCl_2$ (2 equiv)[b]	1:1
5	addition of $MnCl_2$ and under O_2 atmosphere[b]	6:1
6	addition of KO_2 (0.5 equiv)	4:1
7	addition of KO_2 (1 equiv)	10:1
8	addition of KO_2 (2 equiv)[d]	>20:1[e]
9	addition of KO_2 (2 equiv)	1:1
10	addition of KO_2 (1 equiv) and under O_2 atmosphere	>20:1[e]

[a] Standard conditions: **4a** (1.00 mmol in 4 mL CH_3CN, added over 1 h), β-pinene (**9**; 6.00 mmol), MnO_2 (5 mmol), acetic acid (2.00 mmol), CH_3CN (5 mL), rt. [b] Addition of H_2O (0.1 mL) required for solubility of $MnCl_2$. [c] Ratios determined by ^1H NMR analysis. Products further characterized through reduction to the corresponding alcohols with $NaBH_4$ (see the Supporting Information). [d] Standard conditions with 3.00 mmol acetic acid. [e] Hydroperoxide **14** not detected by ^1H NMR spectroscopy.

The origin of the oxygen atoms in the reaction products was determined by hydroperoxyarylation experiments under an atmosphere of ^{18}O-labeled dioxygen and subsequent reduction (Table 5). The exclusive formation of **15*** under $^{18}O_2$ suggests that the dioxygen atmosphere is the only source of the oxygen atom(s) in the hydroperoxides and corresponding alcohols (Table 5, entry 2). However, if hydroperoxyl radicals are present (for example, from the addition of potassium superoxide under slightly acidic conditions), these radicals can compete with the labeled $^{18}O_2$ to give a mixture of **15** and **15*** (Table 5, entry 3). Interestingly, hydroperoxyl radicals have not so far been described as oxygen-centered radical scavengers.

Finally, we investigated the conversion of the now readily available α-hydroperoxycarboxylic acids to chemoluminescent

Table 5. Experiments under $^{18}O_2$ atmosphere.

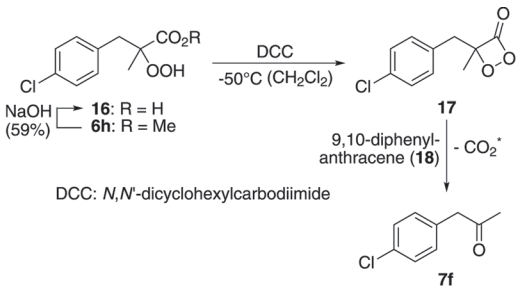


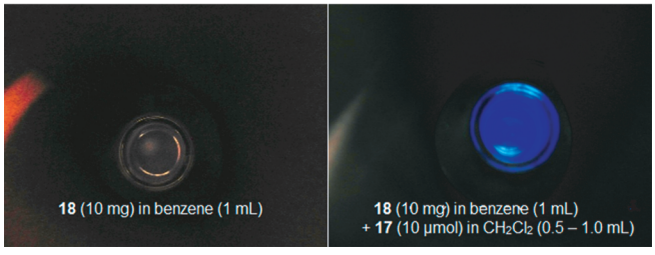
Entry	Conditions[a]	Ratio **15**:**15***[b]
1	control experiment under O_2 atmosphere	only **15**
2	under $^{18}O_2$ atmosphere	only **15***
3	addition of KO_2 (1 equiv) and under $^{18}O_2$ atmosphere	3:1

[a] Standard conditions: **4a** (1.00 mmol in 4 mL CH_3CN, added over 1 h), β-pinene (**9**; 6.00 mmol), MnO_2 (5 mmol), acetic acid (2.00 mmol), CH_3CN (5 mL), rt. [b] Determined by mass spectrometry.

dioxetanones (Scheme 2).[28] Starting from crude hydroperoxyester **6h** (Table 2, entry 8), the acid **16** could be obtained in 59% yield through saponification with aqueous sodium hydroxide. Ring closure with dicyclohexyl carbodiimide at low temperature gave the unstable dioxetanone **17**,[29] which was added in solution to the sensitizer 9,10-diphenylanthracene (**18**)[30] in benzene. Cycloreversion of **17** under simultaneous liberation of photochemically excited carbon dioxide led to ketone **7f** as shown by ^{1}H NMR spectroscopy and TLC.

In summary, we report a new carbooxygenation-type version of the Meerwein arylation in which the introduction of oxygen has been achieved by using dioxygen from the air. In contrast to related reports,[9,11] the best results were obtained with α-substituted acrylates. Importantly, the aryl hydrazine has to be added slowly to the reaction mixture to allow sufficient uptake of dioxygen from the air. Competition and labeling experiments revealed hydroperoxyl radicals as novel oxygen-centered radical scavengers.





Scheme 2. Synthesis of dioxetanone **17** and chemoluminescence experiment.

Experimental Section

General procedure for carbohydroxylations with MnO_2

A solution of aryl hydrazine (1.00 mmol) in acetonitrile (4 mL) was added dropwise over a period of 1 h to a stirred suspension of alkene (6.00 mmol), acetic acid (115 µL, 2.00 mmol), and MnO_2 (435 mg, 5.00 mmol) in acetonitrile (5 mL) at 23 °C. The reaction mixture was filtered and the filter cake was further washed with diethyl ether. The organic layer was washed with water (30 mL) and brine, then dried over Na_2SO_4. The solvents were removed under reduced pressure and the products were purified by flash column chromatography on silica gel.

Acknowledgements

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Keywords: aryl hydrazines · carbooxygenation · dioxygen · hydroperoxyl radicals · radical reactions

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*S. Kindt, H. Jasch, M. R. Heinrich**

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Manganese(IV)-Mediated Hydroperoxyarylation of Alkenes with Aryl Hydrazines and Dioxygen from Air

The introduction of oxygen into a Meerwein arylation has been achieved with dioxygen from air as oxygen-centered radical scavenger. The slow addition of the aryl hydrazine is key to aryl radical formation through oxidation with manganese dioxide; whereby, hydroperoxides were obtained from activated as well as non-activated alkenes.