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Palladium-Catalyzed Selective Acyloxylation Using Sodium Perborate as Oxidant

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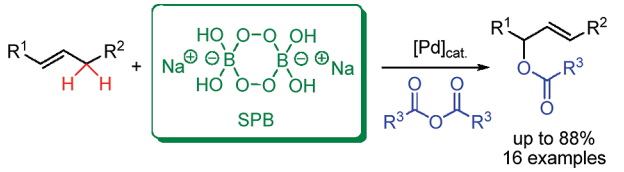

Sodium perborate (SPB), a principal component of washing powders, was employed as an inexpensive and eco-friendly oxidant in the palladium-catalyzed C−H acyloxylation of alkenes in excellent regio- and stereochemistry. The reactions used anhydrides as acyloxy sources. The method applies to both terminal and internal alkenes, and even benzylic C−H oxidation.

Allylic C−H acetoxylation is a synthetically and mechanistically interesting field in palladium catalysis.[1−4] Excellent work by Tsuji,[5] Åkermark,[6,7] Bäckvall,[8,9] McMurry,[10] and Kocovsky[10] established this field in the 90s, with more recent interest by White,[11,12] Stahl,[3,13] Muzart,[14] Kaneda,[15] Stambuli,[16] Bercaw,[17] and ourselves.[18] Early studies focused on finding efficient catalyst systems and reaction conditions. The prevailing system in these studies involved simple palladium salts (e.g., $Pd(OAc)_2$) and benzoquinone (BQ) as essential components and the reactions were performed in AcOH as solvent.[6,10] BQ played a crucial role as an oxidant for Pd(0) and an activator ligand to promote nucleophilic attack.[3,8,9] AcOH was also indispensible for the reduction of BQ to hydroquinone and to provide acetate nucleophiles. This combination was successful in many reactions, but the acidic conditions were problematic for some substrates, which limited synthetic scope. The selectivity of the nucleophilic attack was sometimes unsatisfactory, leading to mixtures of isomers. More recent studies have addressed these problems, varying the solvents and/or increasing the selectivity of the C−H functionalization process.[11−13,16,18] Many of these studies led to the use of new ligand systems and/or alternative oxidants in place of BQ. Recently we published a new solution for palladium-catalyzed C−H acetoxylation and benzoyloxylation of alkenes with $PhI(OAc)_2$ as oxidant, enabling us to replace AcOH with MeCN.[18] We envisioned that the cost and environmental impact would be reduced if $PhI(OAc)_2$ were generated in situ in substoichiometric amounts.[19−21]

The synthesis of $PhI(OAc)_2$ using sodium perborate tetrahydrate (SPB, $NaBO_3 \cdot 4H_2O$),[22] in AcOH reported by Kitamura and co-workers[23] inspired us to use SPB with PhI in our initial attempts to this end. SPB is a cheap (about $2.9/kg,[24] bulk price) and safe oxidant, produced in bulk amounts in the chemical industry (~0.5 million ton/year in EU[25]) and is an important component of washing powder. On its own a weak oxidant, SPB may be activated by AcOH to become a synthetically useful oxidant.[22,26]

Although the palladium-catalyzed C−H acetoxylation of **1a** and **1i** worked well using a SPB/PhI mixture, we quickly found that PhI was superfluous. To avoid AcOH, we used an excess of acetic anhydride (Ac_2O)[26,27] in MeCN solvent to boost the oxidation power of SPB. We found that various alkenes (**1a**−**j**) could be C−H acetoxylated using SPB (**2**) and Ac_2O (**3a**) in the presence of catalytic amounts of $Pd(OAc)_2$ (Scheme 1). Best results were obtained using four equivalents of SPB and 16 equivalents of **3** with respect to the alkene. To the best of our knowledge, this is the first use of **2** as oxidant in palladium catalysis.

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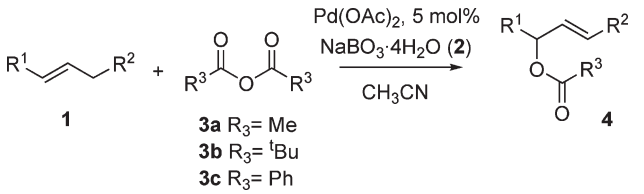
SCHEME 1. Palladium-Catalyzed Acyloxylation of Alkenes Using Sodium Perborate (SPB)



A particular advantage of using SPB (Figure 1) is that it generates nontoxic boric acid and water as byproducts from the oxidation reaction, which also simplifies purification.

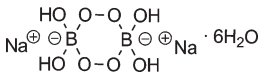


FIGURE 1. Structure of SPB (twice the empirical formula, $NaBO_3 \cdot 4H_2O$).[22,26]

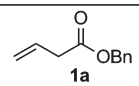
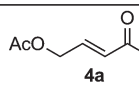
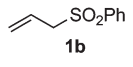
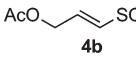
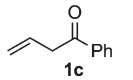
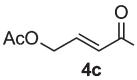
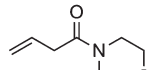
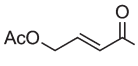
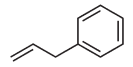
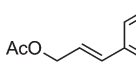
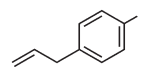
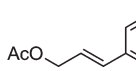
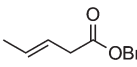
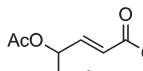
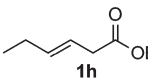
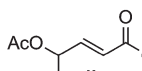
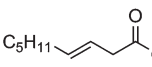
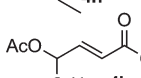
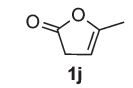
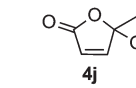
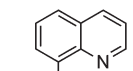
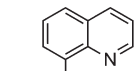
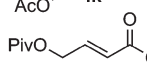
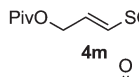
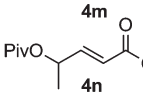
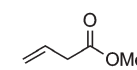
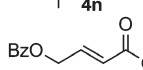
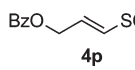
The catalytic reaction proceeds under mild conditions (typically at 40 °C) with high functional group tolerance (Table 1); the ester (entries 1 and 7−9), lactone (entry 10), amide (entry 4) ketone (entry 3), and aromatics (entries 5−6) survived the allylic C−H functionalization unchanged.

A particularly important feature of this procedure is that it is suitable for the C−H functionalization of both terminal (**1a**−**1f**) and internal alkenes (**1g**−**1j**). Without using AcOH as solvent and BQ as oxidant very few efficient C−H acetoxylation methods for oxidation of internal alkenes have been reported in the literature.[3,4] Furthermore, not only allylic but also benzylic C−H bonds[28,29] can be functionalized by the above methodology (entry 11). The benzylic C−H functionalization of **1k** requires harsher conditions than do the allylic C−H bonds; the reaction temperature had to be increased to 100 °C and AcOH used as solvent. Previous studies used $PhI(OAc)_2$ as oxidant under similar reaction conditions for this transformation.[30] Using Piv_2O (**3b**) both terminal and internal alkenes could be functionalized (entries 12−14), and by application of benzoic anhydride (**3c**) benzoyloxylation could be performed (entries 15−16). In these reactions we employed only four equivalents of the corresponding anhydrides.

The reactions were highly selective, giving only one regio- and stereoisomer, with substitution always at the allylic γ-position (relative to the EWG or aryl group) and trans double bond geometry (determined from the ^1H NMR spectrum of the crude reaction mixture) for all acyclic alkene substrates (**1a**−**i** and **1l**). The reactions also proved to be easily scalable. Tenfold scale-ups gave only a small decrease in yields (entries 1 and 13).

Replacing SPB with H_2O_2−urea led to a sharp decrease of the catalytic efficiency. For example, acetoxylation of **1a** with H_2O_2-urea under our standard conditions (entry 1) gave **4a** in only 20% yield. $Na_2S_2O_8$ and Oxone proved to be totally inefficient for the conversion of alkenes (**1**) to allylic acetates under our conditions in absence of SPB. Conducting the reactions using **1**, SPB and Ac_2O in the absence of $Pd(OAc)_2$, we could not detect even traces of allylic acetate products. Under these conditions using internal alkenes (e.g., **1g**) we could detect epoxidation of the double bond,[26,31] in accordance with previous reports using SPB-OAc mixtures

TABLE 1. Palladium-Catalyzed C−H Acyloxylation using SPB as Oxidant[a]

Entry	Substrate	Temp (°C)	Product	Yield (%)
1	 **1a**	40	 **4a**	74/64[b]
2	 **1b**	40	 **4b**	75
3	 **1c**	40	 **4c**	56
4	 **1d**	40	 **4d**	52
5	 **1e**	40	 **4e**	57
6	 **1f**	60	 **4f**	59
7	 **1g**	60	 **4g**	71
8	 **1h**	60	 **4h**	70
9	 **1i**	60	 **4i**	62
10	 **1j**	40	 **4j**	62
11[c]	 **1k**	100	 **4k**	52
12[d]	**1a**	60	 **4l**	72
13[d]	**1b**	60	 **4m**	88/79[b]
14[d]	**1g**	60	 **4n**	58
15[e]	 **1l**	40	 **4o**	62
16[e]	**1b**	60	 **4p**	89

[a]Bn = benzyl; Bz = benzoyl, Piv = pivaloyl. Unless otherwise stated, a mixture of **1** (0.3 mmol), SPB (1.2 mmol), Ac_2O (4.8 mmol) and $Pd(OAc)_2$ (5 mol %) in MeCN (0.5 mL) was stirred for 18 h at the indicated temperature. [b]The reaction is scaled up to 3 mmol of **1**. [c]AcOH used as solvent, reaction conducted for 22 h. [d]Piv_2O (1.2 mmol) was used instead of Ac_2O. [e]Bz_2O (1.2 mmol) was used instead of Ac_2O.

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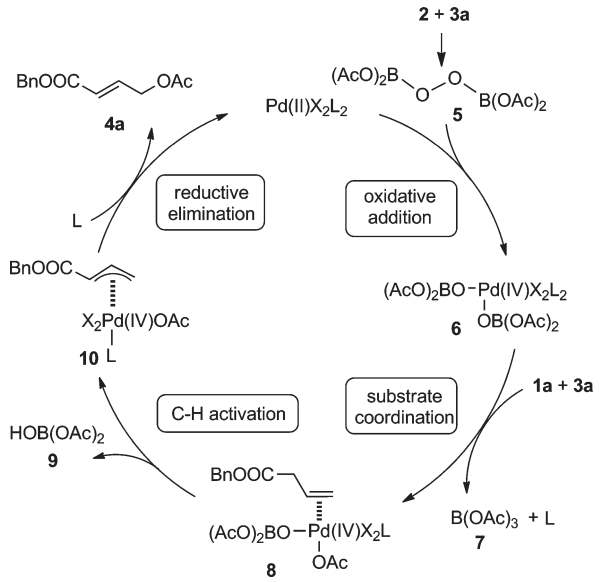

FIGURE 2. Proposed catalytic cycle.

in dichloromethane.[31] However, using $Pd(OAc)_2$ and MeCN as solvent strongly suppresses substrate epoxidation. Analysis of the crude products indicated that for internal alkenes **1g**−**i** traces of epoxy-products were formed, but these could be removed by chromatography. The structure of the ester functionality in **1a**, **1g**−**i**, and **1l** had little effect on the acyloxylation reactions. It affected only the purification of the products. The benzyl esters (**4a**, **4g**, **4h**) are less volatile than the methyl esters reducing the purification losses. When the boiling point of the product (**4i**) is increased by a substituent, the methyl ester was employed. Compared to other products **4k** showed a relatively high tendency for hydrolysis of the acetate, which led to a decrease in yield.

The regio- and stereoselectivity of the reactions are consistent with an allyl-Pd mechanism.[1,2] However, we were unable unambiguously to determine the mechanistic pathway through monitoring the stoichiometric reactivity of model allyl-Pd(II) complexes (see Supporting Information). Accordingly, we recognize that the C−H activation may be occurring through either a Pd(II/IV) catalytic cycle,[30] as postulated for the acetoxylation with $PhI(OAc)_2$,[18] or via the classical Pd(0/II) pathway.

Our proposed mechanism (Figure 2) assumes the first step to be oxidative addition of **5**, formed from the reaction between SPB (**2**) and Ac_2O (**3a**),[31] to the precatalyst (most probably X = OAc, L = MeCN), affording complex **6**. The electron-withdrawing acetate groups in **5** likely encourage conjugation between the peroxide oxygen lone pairs (n_π) and the empty p_π orbital of boron, increasing the oxidation potential. The next steps are boronate−acetate exchange and alkene coordination to give complex **8**, followed by internal deprotonation. The Pd(IV) center in **8** is highly electrophilic, which favors generation of the strongly π-donating η^3-allyl moiety in **10**. Reductive elimination from **10** gives product **4a** with a high regio- and stereoselectivity. A closely related mechanistic alternative could be oxidation of the Pd(II) species by **5** to bimetallic Pd(III) intermediates. A similar oxidative functionalization procedure was reported by Ritter and co-workers[32,33] for pyridine derivatives analogous to **1k**.

The alternative Pd(0)/Pd(II) cycle may begin with the formation of an allyl−Pd(II) complex, subsequently activated by SPB or **5** to give the product and Pd(0), which could be reoxidized by **7**. However, it should be noted that addition of PhI to the reaction mixture does not influence the yield (64%) of the reaction. Our initial studies for in situ generation of $PhI(OAc)_2$ involved addition of PhI in large excess. It is well-known that PhI rapidly undergoes oxidative addition with Pd(0) species but much more reluctantly with Pd(II) species.[34,35] That the active catalyst was not trapped by PhI suggests Pd(0) species might not be catalytically relevant.

In summary, we have described an inexpensive, highly selective catalytic method for the C−H acyloxylation of alkenes using SPB and carboxylic anhydrides. As far as we know, this is the first application of SPB in palladium catalysis. The reaction has a broad synthetic scope and it can be used for both external and internal alkenes and benzylic acetoxylation. The acyloxy groups can be varied by selecting different anhydrides. The products of the catalytic C−H functionalization reactions can be employed as useful substrates in palladium-catalyzed allylic substitution reactions.[1,2] The C−H functionalization of internal alkenes suggests a large potential for asymmetric induction, for which few efficient protocols currently exist.

Experimental Section

General Method A. Acetoxylation of Alkenes. A mixture of $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 5 mol%), SPB, **2** (185 mg, 1.2 mmol), MeCN (0.5 mL), anhydride **3a** (489 mg, 4.8 mmol), and **1** (0.3 mmol) in a screwtop vial was stirred for 18 h at the indicated temperature. The crude was partitioned between water (10 mL) and Et_2O (10 mL), washed with water (3 × 10 mL), dried ($MgSO_4$), filtered, concentrated, and purified by column chromatography.

General Method B. Pivaloylation and Benzoylation of Alkenes. The reactions were performed as in general method A except pivalic acid anhydride (1.2 mmol) or benzoic acid anhydride (1.2 mmol) were used. One ml of MeCN was used instead of 0.5 mL and saturated aqueous $NaHCO_3$ was used instead of water in the work up.

(*E*)-3-(Phenylsulfonyl)Allyl Acetate (4b): Synthesized according to general method A. Isolated by column chromatography (Et_2O/pentane 1:3) as a colorless oil (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10 (3H, s), 4.77 (2H, dd, $^3J_{HH}$ = 4.0 Hz, $^4J_{HH'}$ = 2.0 Hz), 6.56 (1H, dt, $^3J_{HH}$ = 15.1 Hz, 2.0 Hz), 6.98 (1H, dt, $^3J_{HH}$ = 15.1, 4.0 Hz), 7.52−7.59 (2H, m), 7.61−7.67 (1H, m), 7.87−7.92 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 61. 6, 127.9, 129.5, 131.4, 133. 8, 139.6, 140.0, 170.0. HRMS (ESI): *m*/*z* calcd. for $[C_{11}H_{12}O_4S + Na]^+$ 263.0349, found 263.0355.

(*E*)-4-Morpholino-4-oxobut-2-en-1-yl Acetate (4d): Synthesized according to general method A without aqueous workup. Isolated by column chromatography (EtOAc) as a colorless oil (52%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.11 (3H, s), 3.50−3.76 (8H, m), 4.74 (2H, dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.8 Hz), 6.43 (1H, dt, $^3J_{HH}$ = 15.2 Hz, $^4J_{HH}$ = 1.8 Hz), 6.86 (1H, dt, $^3J_{HH}$ = 15.2,

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5.1 Hz).^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 42.5, 46.4, 63.3, 66.9 (two overlapping signals, see attached HSQC spectrum in Supporting Information), 121.3, 139.0, 164.9, 170.5. HRMS (ESI): m/z calcd. for $[C_{10}H_{15}NO_4 + Na]^+$ 236.0893, found 236.0896.

(***E***)**-Benzyl 4-acetoxyhex-2-enoate (4h):** Synthesized according to general method A. Isolated by column chromatography (Et_2O/pentane 1:5) as a colorless oil (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (3H, t, $^3J_{HH}$ = 7.4 Hz), 1.64−1.75 (2H, m), 2.09 (3H, s), 5.18 (2H, s), 5.48 (1H, m), 5.99 (1H, dd, $^3J_{HH}$ = 15.8 Hz, $^4J_{HH}$ = 1.6 Hz), 6.88 (1H, dd, $^3J_{HH}$ = 15.8, 5.29 Hz), 7.30−7.40 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.4, 21.1, 27.0, 66.6, 121.4, 128.5, 128.7, 135.9, 146.0, 166.0, 170.2. HRMS (ESI): m/z calcd. for $[C_{15}H_{18}O_4 + Na]^+$ 285.1097, found: 285.1101.

5-(Acetyloxy)-5-methyl-2(5*H*)-furanone (4j): Synthesized according to general method A. Isolated by column chromatography (EtOAc/pentane 1:5) as a colorless oil (62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.82 (3H, s), 2.08 (3H, s), 6.17 (1H, d, $^3J_{HH}$ = 5.7 Hz), 7.62 (1H, d, $^3J_{HH}$ = 5.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 23.0, 107.1, 122.9, 153.3, 168.9, 169.3. HRMS (ESI): m/z calcd. for $[C_7H_8O_4 + Na]^+$ 179.0315, found 179.0320.

(***E***)**-Benzyl 4-pivaloxybut-2-enoate (4l):** Synthesized according to general method B. Isolated by column chromatography (Et_2O/pentane 1:4) as a colorless oil (72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.24 (9H, s), 4.73 (2H, dd, $^3J_{HH}$ = 4.4 Hz, $^4J_{HH}$ = 2.1 Hz), 5.20 (2H, s), 6.07 (1H, dt, $^3J_{HH}$ = 15.8 Hz, $^4J_{HH}$ = 2.1 Hz), δ 7.00 (1H, dt, $^3J_{HH}$ = 15.8 Hz, 4.4 Hz), δ 7.30−7.41 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.3, 39.0, 62.6, 66.6, 121.5, 128.5, 128.7, 135.9, 142.4, 165.8, 177.9. HRMS (ESI): m/z calcd. for $[C_{16}H_{20}O_4 + Na]^+$ 299.1254, found 299.1268.

(***E***)**-3-(phenylsulfonyl)allyl Pivalate (4m):** Synthesized according to general method B. Isolated by column chromatography (Et_2O/pentane 2:3) as a colorless oil (88%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.20 (9H, s), 4.76 (2H, dd, $^3J_{HH}$ = 4.0 Hz, $^4J_{HH}$ = 2.1 Hz), 6.52 (1H, dt, $^3J_{HH}$ = 15.1, $^4J_{HH}$ = 2.1 Hz), 7.00 (1H, dt, $^3J_{HH}$ = 15.1, 4.0 Hz), 7.55 (2H, tm, $^3J_{HH}$ = 7.8 Hz), 7.64 (1H, tm, $^3J_{HH}$ = 7.4 Hz), 7.89 (2H, dm, $^3J_{HH}$ = 7.3, 1.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.3, 39.0, 61.6, 127.9, 129.5, 131.2, 133.8, 140.0, 140.2, 177.6. HRMS (ESI): m/z calcd. for $[C_{14}H_{18}O_4S + Na]^+$ 305.0818, found 305.0806.

(***E***)**-Benzyl 4-pivaloxypent-2-enoate (4n):** Synthesized according to general method B. Isolated by column chromatography (Et_2O/pentane 1:9) as a pale yellow oil (58%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.22 (9H, s), 1.34 (3H, d, $^3J_{HH}$ = 6.7 Hz), 5.19 (2H, d, $^3J_{HH}$ = 2.5 Hz), 5.47 (1H, m), 5.99 (1H, dd, $^3J_{HH}$ = 15.8 Hz, $^4J_{HH}$ = 1.8 Hz), 6.93 (1H, dd, $^3J_{HH}$ = 15.8, 4.6 Hz), 7.30 − 7.41 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 27.3, 39.0, 66.6, 68.6, 120.4, 128.5, 128.5, 128.7, 136.0, 147.5, 166.1, 177.6. HRMS (ESI): m/z calcd. for $[C_{17}H_{22}O_4 + Na]^+$ 313.1410, found 313.1396.

(***E***)**-3-(phenylsulfonyl)allyl Benzoate (4p):** Synthesized according to general method B. Isolated by column chromatography (Et_2O/pentane 1:1) as a colorless oil (89%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.05 (2H, dd, $^3J_{HH}$ = 4.0 Hz, $^4J_{HH}$ = 2.1 Hz), 6.65 (1H, dt, $^3J_{HH}$ = 15.2 Hz, $^4J_{HH}$ = 2.1 Hz), 7.12 (1H, dt, $^3J_{HH}$ = 15.2, 4.0 Hz), 7.46 (2H, t, $^3J_{HH}$ = 7.7 Hz), 7.52−7.65 (4H, m), 7.91 (2H, dm, $^3J_{HH}$ = 7.1 Hz), 8.03 (2H, dm, $^3J_{HH}$ = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 62.0, 128.0, 128.7, 129.2, 129.5, 129.9, 130.3, 131.5, 133.7, 133.8, 139.9, 140.0, 135.6. HRMS (ESI): m/z calcd. for $[C_{16}H_{14}O_4S + Na]^+$ 325.0510, found 325.0507.

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Supporting Information Available: General experimental details and spectroscopic data for the acyloxylation products. This material is available free of charge via the Internet at http://pubs.acs.org.