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lodine(III)-catalyzed benzylic oxidation by using the (PhIO)_n/Al(NO₃)₃ system

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ABSTRACT

The first iodine(III)-based procedure for the benzylic oxidation of different arenes is described by using the (PhIO)_n/Al(NO₃)₃ system under catalytic conditions leading to the formation of the corresponding carbonyl derivatives. The method proceeds under mild, operationally simple, room temperature, short reaction times, and open flask conditions. In light of the organocatalysis relevance and the novelty of our protocol, we wish to communicate our initial results of this novel oxidation.

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KEYWORDS

Benzylic oxidation; C_{sp}³-H activation; iodine(III)catalysis; organocatalyst

GRAPHICAL ABSTRACT



Introduction

Benzylic oxidation is an excellent strategy for direct access to a wide range of benzylic functional groups. Regarding the oxygen atom introduction at this position, different strategies have been applied for the direct C_{sp}^{3} -H activation leading to the formation of carbonyl derivatives as a final product. Protocols involving metal-catalyzed reactions

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Scheme 1. Representative iodine(III) or (V)-base procedures for the benzylic oxidation.

using Cu(I)^[1] and Cu(II),^[2] Co(II),^[3] Rh(II),^[4] Fe(II)^[5] and Fe(III),^[6] Pd(II),^[7] Mg(II),^[8] Mn(II)^[9] or Ni(II)^[10] has been described to carry out the benzylic oxidation. On the other hand, metal-free oxidative procedures with persulfates and pyridine $(K_2S_2O_8/Py)$,^[11] molecular oxygen and *n*-octylphosphinate [PhP(O)H(Onoctyl)/O2]^[12] or potassium bromide and Oxone®^[13] were successfully applied. Finally, in the context of this work, few protocols using hypervalent λ^3 or λ^5 iodanes have been described under stoichiometric conditions. Among them, the procedure of Kita [(PhIO)n-KBr],^[14] Telvekar (PIDA-NaN₃),^[15] or Nicolaou (IBX-H₂O)^[16] are the most representatives (Scheme 1).

All of these procedures showed the carbonyl formation at the benzylic position in good yields. However, important disadvantages that are pointed out are high temperatures or long reaction times; nevertheless, the biggest issue is the use of stoichiometric amount of oxidant, which can be as far as ten times with respect to the benzylic alkane. The former issue may indicate the generation of a soft-oxidant which needs a considerable excess to carry out the carbonyl formation. Herein, we present our initial findings in the development of benzylic oxidation, catalyzed by monomeric iodosylbenzene (PhIO) in redox-neutral conditions using the aluminum nitrate as an oxidant. To the best of our knowledge, there are no catalytic procedures for the direct synthesis of

	H H O 9 <i>H</i> -xanthene	(PhIO) _n , Al(NO ₃) ₃ ·9H ₂ O → solvent, 23 °C	9H-xanthen-9-one	
Entry	(PhIO) _n (equiv)	Al(NO ₃) ₃ (equiv)	Solvent	Yield (%) ^b
1	0.25	0.35	MeCN	73
2	0.20	0.35	MeCN	68
3	0.30	0.35	MeCN	71
4	0.25	0.40	MeCN	55
5	0.25	0.30	MeCN	62
6	0.25	0.35	1,2-DCE	n.r.
7	0.25	0.35	THF	Dec.
8	0	0.35	MeCN	n.r.
9	0.25	0	MeCN	n.r.
10 ^c	0.25	0.35	MeCN	n.r.

Table 1. Optimization of the PhIO-catalyzed benzylic oxidation of 9 H-xanthene.^a

^aReaction conditions: solvent (0.3 M), open flask;

^bisolated yields;

^cPhI was used instead of (PhIO)_n.

benzylic carbonyls via the direct C_{sp}^{3} -H oxidation without a sequential route that involves more than one step using iodine(III) reagents.

Results and discussion

Recently, our group discovered a novel reactivity of different iodine(III) reagents by combining with different aluminum as well as ammonium halogen salts. This combination was applied for the chlorination, bromination, and iodination of arenes, mainly phenols. This new reactivity is chemically supported on the direct coordination of the aluminum with the ligand of the hypervalent iodine(III) reagent. The interaction generates an oxidative system such as PIFA-AlCl₃,^[17] PIDA-AlBr₃,^[18] or polymeric iodosylbenzene (PhIO)_n-AlCl₃/AlBr₃,^[19] which finally transfers the group bonded to the aluminum to the arene. In the former study, we described the aluminum-mediated depolymerization of (PhIO)_n into its monomeric unit (PhIO) leading to the in situ formation of the active species. Additionally, we observed the same depolymerization reaction by using the corresponding ammonium chloride, bromide, and iodide salts.^[20] In line with this strategy, with regard to the combination of iodine(III)-AlX₃ (X=Cl, Br, I), we described the nitration of different phenols using aluminum nitrate as the source of nitro group.^[21] During the development of this protocol, we tested the 9H-xhantene. Surprisingly, we found the oxidative C_{sp}³-H bond transformation to its corresponding carbonyl group under the catalytic conditions at the Iodine(III) reagent. Thus, it was decided to explore and optimize this unexpected transformation using the same substrate (Table 1).

The first conditions involved 0.25 equivalent of polymeric iodosylbenzene and 0.35 equivalent of aluminum nitrate in acetonitrile to obtain the corresponding 9H-xanthen-9-one in 73% of the yield (entry 1). Systematically, we started to vary the iodine(III)

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source. Thus, by decreasing the iodosylbenzene equivalents to 0.2, a lower 68% of yield was observed (entry 2). According to this experiment, we rationalized that less amount of polymeric iodosylbenzene would continue decreasing the obtained yield. In consequence, we increased to 0.3 equivalent of polymeric iodosylbenzene and we found again a higher yield with almost the initial result (71%, entry 3). These experiments indicated that 0.25 equivalents of polymeric iodosylbenzene is the optimal amount in the reaction. Additionally, it is possible to mention that the reaction proceeds under *catalytic conditions at the iodine(III) reagent*. On the other hand, the use of 0.4 or 0.3 equivalents of aluminum nitrate (entries 4 and 5) showed lower 55 and 62% yields, respectively; by comparing with entry 1. Other solvents such as 1,2-DCE or THF (entries 6 and 7) were tested, however, no reaction or decomposition was found. To finish this optimization, control experiments in the absence of polymeric iodosylbenzene, aluminum nitrate or by using iodobenzene as a plausible oxidant precursor were carried out (entries 8–10), nevertheless, no reaction was found.

^aReaction conditions: MeCN (0.3 M), open flask and 2–4 h.

^bIsolated yields.

This series of experiments determined the conditions in entry 1 as the optimal for the benzylic oxidation and carbonyl formation.

With the optimized conditions at hand, we proceeded to explore the scope of this reaction (Table 2).

The scope exploration started with the oxidation of mono-annular phenols and phenol-ethers such as 1-ethyl-4-methoxybenzene and 4-(methoxymethyl)phenol. Under our optimized conditions, 78 and 62% (entries 1 and 2) of yield, respectively of the carbonyl group formation at benzylic position was obtained for 1 and 2. In these two examples, the arene moiety which contains the electron-donating groups (-OMe and -OH) did not affect the expected reactivity, nevertheless, this former example is the electron-richer which displays the lower yield. Other bis-annular arenes such as indene and isochromane were successfully tested, giving rise to 3 and 4 in 66 and 82% of yield, respectively (entries 3 and 4). Regarding these examples, it is worth to highlight that the oxidation of the electron-neutral C_{sp}³-H bonds proceeded in modest yield in the five-member ring of the indene, while in the electron-rich C_{sp}^{3} -H bonds of the six-member ring of the isochromane, the reaction proceeded in a much higher yield. The systematic scope exploration continued with the oxidation of tris-annular arenes. In such a way, the anthracen-9(10H)-one, 9H-fluorene, and the optimized 9H-xanthene were oxidized at the benzylic position, leading to the formation of the corresponding benzylic carbonyls 5, 6, and 7 in 46, 58, and 73% of yield, respectively (entries 5-7). In these three experiments, it is remarkable again, while the electron-richer is the benzylic C_{sp}³-H bond, the yield increases, thus a direct correlation between the electronic nature and the desired reactivity at the benzylic position was observed.

Considering the results, it was decided to test other benzylic mono-annular derivatives containing electron-donating groups such as phenyl and methoxyl at the arene moiety and a benzylic methoxyl group. Surprisingly, the cleavage of the benzylic methoxy group with concomitant over-oxidation to the corresponding carboxylic acid group was observed giving rise to the compounds **8** and **9** in 34 and 38%, respectively (entries 8 and 9). It is important to point out, these former examples contain the most electron-rich benzylic C_{sp}^{3} -H bonds since they are bonded to two (entry 8) or three (entry 9) electron-donating groups.

The results in this set of experiments clearly indicated that electron-rich arenes mainly react toward the benzylic C_{sp}^{3} -H oxidation instead of C_{sp}^{2} -H nitration.^[21] However, the arenes strongly activated with electron-rich groups (–OH, two –OMe or –Ph) will decrease the yield of the carbonyl formation or will show overoxidation to the carboxylic acid. This implies an electron-dependent benzylic oxidation with a *moderate activation* at the arene fragment.

Several other compounds containing electron-attracting substituents, electron-neutral groups, saturated *N*-heterocycles at the arene moiety or the pyridine nucleus, did not react under our catalytic oxidation conditions. In the case of the saturated *N*-heterocycles and the pyridine, the absence of reactivity is attributed to the Lewis basicity of the nitrogen. The rest of the tested substrates lack arene activation and in consequence, no reaction was observed.

Finally, a mechanistic proposal of this novel oxidation is outlined (Scheme 2).



Scheme 2. Proposed catalytic cycle for the PhIO-catalyzed benzylic oxidation.

The reaction started with the coordination of aluminum nitrate to polymeric iodosylbenzene to get the adduct $(PhIO)_n$ -Al $(NO_3)_3$. This depolymerizes giving rise to I. The following radical fragmentation of I leads to the formation of II and III (radical nitrite). The radical nitrite III promotes the hydrogen atom transfer (HAT) from the benzylic arene leading to the formation of nitrous acid and the benzylic radical IV. Here, the radicals IV and II gets coupled to form V. This intermediate reacts with the nitrite anion formed, to produce the tetra-coordinated aluminum species VI. This intermediate undergoes fragmentation giving rise to the corresponding benzylic alcohol, a mixed aluminum salt containing the nitrate and nitrite anions with concomitant formation of monomeric iodosylbenzene. At this point, the mixed aluminum salt reacts with the iodosylbenzene producing more nitrite radicals as well as those of type II which can contain nitrate or nitrate and nitrite anions. In such a way, the catalytic cycle continues following the path A or Path B. The path A gives rise to more benzylic alcohol; on the other hand, the path B started by a second HAT from the benzylic alcohol with the nitrite radical forming VIII that reacts with II producing the adduct IX. The following coordination to the aluminum center in IX gives rise to X which finally after fragmentation, generates the mixed aluminum salt XI monomeric iodosylbenzene and yields the observed carbonyl compound.

Additional theoretical and experimental details regarding this novel transformation are currently been studied in our laboratory.

Conclusions

In summary, we have developed the first iodine(III)-catalyzed benzylic oxidation of electron rich-arenes which are moderately activated by electron-donating groups. The procedure is cost-economic since it needs only 0.35 equivalent of aluminum nitrate as an oxidant. The protocol proceeds at room temperature and open flask conditions in only 2–4 hours.

To the best of our knowledge, this is the first report describing an organocatalytic benzylic oxidation, using hypervalent iodine(III) as a redox-neutral catalyst.

Experimental

General procedure

In a 25 ml dry round-bottom flask was suspended polymeric PhIO (0.25 equivalent) in dry acetonitrile at 23 °C. Then, Al(NO₃)₃ (0.35 equivalent) was added and stirred for 10 min, afterward, it was cooled to 0 °C. The benzylic aryl derivative (1 equivalent) was incorporated in one portion. The reaction was warmed to 23 °C for a period of 2–4 h until the starting material was fully consumed judging its advance by TLC. The reaction mixture was quenched by the addition of NH₄Cl saturated solution (25 mL) and then extracted with EtOAc (3 × 10 mL). The organic extracts were collected, dried over anhydrous sodium sulfate, filtered, and concentrated in *vacuo* to remove the solvent and yield the crude of the reaction. The product was purified by flash column chromatography on silica gel (100–200 mesh) with EtOAc/hexane system.

Selected spectroscopic data

Methyl 4-hydroxybenzoate (2)

White solid (62% yield); m.p. 126–128 °C; ¹H NMR (495 MHz, CDCl₃) δ 7.99 (d, J=9.0 Hz, 1 H), 6.91 (d, J=9.0 Hz, 1 H), 3.88 (s, 2 H), 3.85 (s, 2 H); ¹³C NMR (125 MHz, CDCl₃) δ .167.0, 163.4, 131.7, 122.7, 113.7, 55.5, 52.0. IR (neat) ν/cm^{-1} : 3321, 2986, 1709, 1601, 1516, 1428, 798. HRMS (ESI–) calcd. for C₈H₇O [M–H]: 151.0395, found 151.0403.^[14]

2,3-dihydro-1H-inden-1-one (3)

Light yellow solid (66% yield); m.p. 37–38 °C; ¹H NMR (495 MHz, CDCl₃) δ 7.77 (dd, J = 7.7, 0.5 Hz, 1H), 7.59 (td, J = 7.6, 1.2 Hz, 1H), 7.52–7.46 (m, 1H), 7.40–7.35 (m, 1H), 3.15 (t, J = 5.0 Hz, 2H), 2.73–2.67 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 207.3, 155.3, 137.2, 134.7, 127.4, 126.8, 123.9, 36.4, 25.9. IR (neat) ν/cm^{-1} : 2952, 1655, 1560, 1475,

1230, 1333, 720. HRMS (ESI+) calcd. for C_9H_9O [M+H]: 133.0653, found 133.0648.^[14]

Isochroman-1-one (4)

Colorless oil (82% yield); ¹H NMR (495 MHz, CDCl₃) δ 8.11 (dd, J = 7.8, 0.5 Hz, 1H), 7.54 (td, J = 7.5, 1.0 Hz, 1H), 7.44–7.36 (m, 1H), 7.30–7.25 (m, 1H), 4.74–4.44 (m, 1H), 3.07 (t, J = 6.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 165.2, 139.7, 133.8, 130.5, 127.8, 127.4, 125.4, 67.4, 28.0. IR (neat) ν/cm^{-1} : 1730, 1601, 1444, 1399, 1266, 1248, 1098, 1003, 918, 735, 675. HRMS (ESI+) calcd. for C₉H₉O₂ [M+H]: 149.0603, found 181.0674.^[22]

9H-xanthen-9-one (5)

White solid (73% yield); m.p. 177–178 °C; ¹H NMR (495 MHz, CDCl₃) δ 8.35 (dd, J = 8.0, 1.7 Hz, 1H), 7.79–7.66 (m, 1H), 7.49 (dd, J = 8.4, 0.8 Hz, 1H), 7.38 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 177.3, 156.3, 134.9, 126.9, 124.0, 122.0, 118.1. IR (neat) ν/cm^{-1} : 2962, 1670, 1556, 1486, 14, 1323, 760. HRMS (ESI+) calcd. for C₁₃H₉O₂ [M + H]: 197.0603, found 187.0621.^[22]

9H-fluoren-9-one (6)

Yellow solid (58% yield); m.p. 74–76 °C; ¹H NMR (495 MHz, CDCl₃) δ 7.68–7.64 (m, 1H), 7.54–7.45 (m, 2H), 7.29 (td, J=7.3, 1.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 194.0, 144.6, 134.8, 134.3, 129.2, 124.5, 120.4. IR (neat) ν /cm⁻¹: 1711, 1613, 1446, 1293, 955, 737, 658. HRMS (ESI+) calcd. for C₁₃H₉O [M + H]: 181.0653, found 181.0650.^[22]

Anthracene-9,10-dione (7)

Yellow crystals (46% yield); m.p. 284–286 °C; ¹H NMR (495 MHz, CDCl₃) δ 8.32 (dd, J = 5.8, 3.3 Hz, 1H), 7.80 (dd, J = 5.8, 3.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 183.3, 134.3, 133.7, 127.4. IR (neat) ν/cm^{-1} : 1677, 1566, 1346, 1278, 914, 756, 701. HRMS (ESI+) calcd. for C₁₄H₉O₂ [M+H]: 209.0603, found 181.0615.^[22]

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Disclosure statement

The authors declare no competing financial interest.

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