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Oxidative cyclization of alkenoic acids promoted by AgOAc†

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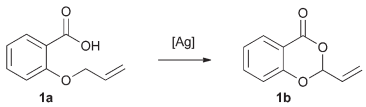
Alkenoic acids derived from salicylic acid and analogues undergo an unexpected oxidative cyclization process triggered by AgOAc leading to 4*H*-benzo[*d*][1,3]dioxin-4-ones. The process is affected by the substitution on the aryl and the allyl units.

The oxidation of a C–H bond at an allylic position is one of the most general examples of C–H bond functionalization due to the activation of the adjacent double bond. This transformation has been achieved by different approaches; traditional methods employ reagents of selenium or chromium but it can also be performed with complexes of Mn, Ru, Co, Rh, Pd, Cu and other metal free procedures.[1,2] In spite of the efforts made to develop increasingly milder and efficient methods, some of the drawbacks still associated with this reaction are with respect to selectivity, functional group compatibility, toxicity and the cost of the reagents. Herein we report that AgOAc, a relatively cheap and non-toxic reagent, is able to execute the oxidative cyclization of alkenoic acids at an allylic position, rendering 4*H*-benzo[*d*][1,3]dioxin-4-one type compounds. Similar oxidative cyclization processes have been described before with Pd(II) leading to lactones,[3] oxazolidinones, and imidazolidinones,[4] but to the best of our knowledge this is the first time that such a type of reactivity is described for Ag. The closer examples of C–H bond functionalization mediated by Ag that afford a new C–X bond are the hydrocarbon oxidations described by Crivello,[5] the C–H functionalization C/O cyclization described by Xu, and the C–H aminations described by the groups of Pérez, He, Schomaker, and Shi.[6]

As an extension of our previous work on cycloisomerization of alkynoic acids[7] we wanted to explore if alkenoic acids undergo similar cycloisomerization processes. Taking alkenoic acid **1a** as a model, we first examined the reactivity of this substrate under the conditions optimized for the cycloisomerization of alkynoic acids with Ag(I) (Table 1, entry 1), but no reaction was observed. This was not surprising, as cycloisomerization reactions of alkenes with silver are more challenging than with alkynes and usually require higher temperatures and longer reaction times.[8] We next replaced the silver source with AgOAc, and changed the reaction conditions increasing the amount of silver up to 1 equivalent and heating at 100 °C for 18 h in DMSO. Unexpectedly under these conditions **1a** led to 4*H*-benzo[*d*][1,3]dioxin-4-one **1b** in 29% yield (entry 2), which formally comes from an oxidative cyclization process at the allylic position, instead of a cycloisomerization reaction. This direct C–O bond forming reaction is unusual for Ag(I) under the conditions employed, since the related C–X bond forming reactions with Ag(I) require the presence of an oxidant.[5,6] 4*H*-Benzo[*d*][1,3]dioxin-4-ones, besides being used

Table 1 Optimization of the oxidative cyclization of **1b** with Ag(I)[a]



Entry	[Ag] (equiv.)	Solvent	T (°C), t (h)	Yield **1b**[b] (%)
1	$AgSbF_6/PPh_3$ (0.05/0.05)	DCE	70, 16	—
2	AgOAc (1)	DMSO	100, 18	29
3	AgOAc (1)	DMSO	120, 18	35
4	AgOAc (2)	DMSO	120, 18	52
5	AgOAc (3)	DMSO	120, 18	74
6	AgOAc (3)	DMF	120, 21	40
7	AgOAc (3)	C_2H_5CN	90, 18	—
8	AgOAc (3)	DCE	80, 18	—
9	AgOAc (3)	Toluene	100, 18	—
10	AgOAc (3) PPh_3 (1)	DMSO	120, 18	40
11	(IPr)AgOAc (3)	DMSO	120, 18	—
12	Ag_2O (3)	DMSO	120, 18	<5[c]
13	$AgNO_3$ (3)	DMF	120, 18	29
14	Ag_2CO_3 (2)	DMSO	120, 18	33
15	$AgCO_2CF_3$ (3)	DMSO	120, 24	—

[a] Reaction conditions: **1a** (0.08 mmol ml^{-1}). [b] Isolated yield. [c] Yield determined by ^1H NMR.

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as useful intermediates in organic synthesis,[9] are present in insecticides[10] and compounds with anti-inflammatory,[11] anti-ulcer,[12] and antimicrobial[13] activities. They have previously been prepared by condensation of salicylic acid derivatives with aldehydes and ketones,[14] substitution of salicylic acid derivatives onto dichloromethane[15] and by iodoaromatization of enyne-dioxinones.[16]

With the aim of optimizing and understanding this transformation we undertook a series of experiments (Tables 1 and 2). An increase of the temperature to 120 °C slightly raised the yield to 35% (Table 1, entry 3), while the addition of two and three equiv. of AgOAc, at this temperature, enhanced the yields to 52% and 74% respectively (entries 4 and 5). In less polar solvents (entries 6–9), the reaction did not proceed or proceeded with lower yields (40% in DMF, entry 6). Other Ag(I) salts, including Ag_2CO_3 that is successfully used in the Fétizon's oxidation,[17] gave lower yields (entries 12–15). Remarkably, it could be observed that the basicity of the counteranion affected the yield of **1b**. In order to improve the solubility of AgOAc, we studied the effect of adding 1 equiv. of PPh_3 (entry 10) and the activity of the complex IPrAgOAc,[18] in which the silver atom is coordinated to a carbene ligand (entry 11). In the former case the yield lowered to 40%, while in the latter the reaction did not take place, in spite of being homogeneous.

Next, we examined the reaction in the presence of different bases to study if the proton at the allylic position could be removed with the assistance of an external base. However, the addition of inorganic as well as organic bases of different basicities either had no effect or lowered the reaction yields (Table 2). Thus, when using 1 equiv. of AgOAc in the presence of 2 equiv. of NaOAc or DABCO, the yield was of the same order as in the absence of base (entries 1 and 6). Employing AgOAc (1 equiv.) with NH_4OAc (2 equiv.) as the base, or DMAP (3 equiv.) in the presence of AgOAc (3 equiv.) the yield decreased to 11% and 23% respectively (entries 2 and 8). Finally, in the case of Cs_2CO_3 and K_2CO_3 the reaction was inhibited (entries 3 and 4), as was the case with the organic bases Et_3N and K*t*BuO (entries 5 and 7).

From the above experiments, the best conditions found for the oxidative cyclization of **1a** were 3 equiv. of AgOAc in DMSO at 120 °C for 18 h (Table 1, entry 5). Using these optimized conditions, we studied the scope of the reaction on a series of alkenoic acids with different substitution patterns. π donor substituents onto the phenyl ring at the *para* position with respect to the carboxylic acid, 4-OMe and 4-Cl (substrates **2a** and **3a**, Table 3, entry 1), lowered the cyclization yield to 44% and 36%, respectively. Alkenoic acid **4a** with a 3-Me group cyclized in 65% yield, whereas alkenoic acid **5a** containing a 5-OMe group cyclized in 60% yield (entry 1). Electron-withdrawing groups at the *para* position with respect to the allyl moiety (5-Cl and 5-NO_2) rendered a side reaction, the decarboxylation of the carboxylic group. In the case of 5-Cl, the product coming from the oxidative cyclization (**6b**) and the product of decarboxylation (**6c**) were both formed in 32% yield, while with 5-NO_2 only the decarboxylation product **7c** was observed in 65% yield (entry 2). The compatibility of the method with a free hydroxy group susceptible of undergoing the Fétizon's oxidation was studied on substrate **8a**. In this case the cyclization product **8b** was obtained in low yield (4%) along with the decarboxylation product **8c** in 7% yield (entry 3). The reaction over the naphthoic acid **9a** led to the tricyclic compound **9b** in 50% yield (entry 4). Next the effect of replacing the oxygen atom at the *ortho* position of the carbonyl group by an atom of sulphur and a NTs group was studied. In the case of sulphur, the cyclization yield increased to 84%, whereas with the NTs group the yield was 67% (entry 5). The result of adding substituents at the allyl moiety was studied as well on alkenoic acids **12a–16a**. It was observed that the addition of a methyl group at the methylene of the allyl unit dropped the yield to 20% for X = O while for X = S the yield was 47% (entry 6). On the other hand, substitution of the olefin with a phenyl group at the terminal carbon atom favoured the decarboxylation pathway leading to **14c** in 58% yield, while the introduction of two methyl groups resulted in the decomposition of alkenoic acids **15a** and **16a** (entry 7). We examine the relevance of the carboxylic acid in the C–H activation, evaluating the reactivity of sulfonamide **17a** and allyl-phenyl ether (**18a**). However none of these compounds reacted, indicating that the acidic carbonyl group is essential for the reaction to proceed (entry 8). Additionally, in order to verify if the reaction worked with other activated methylenes, the cyclization of benzoic acid **19a** bearing a benzyl group was examined. In this case, only the decarboxylation product **19c** was obtained in 81% yield (entry 9). Finally, we tested the reaction on the linear alkenoic acid **20a** (entry 10). Nonetheless, it was recovered unaltered showing that the presence of the phenyl ring is necessary to enforce the proximity of the reacting moieties.

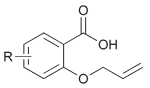
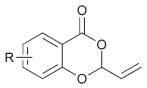
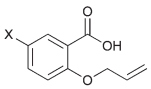
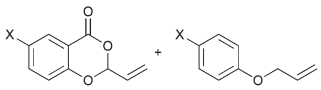
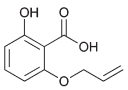
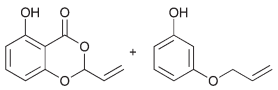
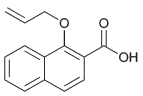
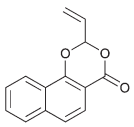
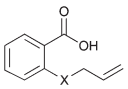
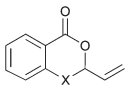
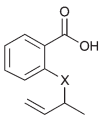
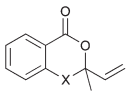
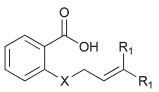
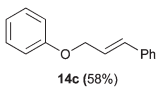
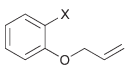
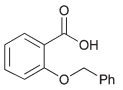
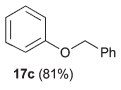
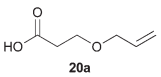
Table 2 Oxidative cyclization of **1b** in the presence of bases[a]

Entry	AgOAc (equiv.)	Base (equiv.)	*T* (°C), *t* (h)	Yield[b] (%)
1	1	NaOAc (2)	120, 24	36
2	1	NH_4OAc (2)	120, 18	11
3	1	K_2CO_3 (2)	120, 18	—
4	1	Cs_2CO_3 (2)	120, 18	—
5	1	K*t*BuO (2)	120, 18	—
6	1	DABCO (2)	120, 18	30
7	3	Et_3N (2)	80, 22	—
8	3	DMAP (3)	120, 18	23

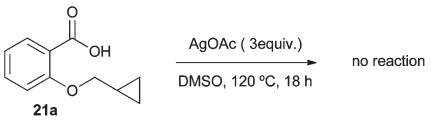
[a] Reaction conditions: **1a** (0.08 mmol ml^{-1}), solvent = DMSO. [b] Isolated yield.

In order to study the reaction mechanism several experiments were undertaken. Monitoring the reaction in DMSO-d_6, we could observe that initially an acid–base ligand exchange between AgOAc and **1a** takes place to form a Ag(I)-benzoate in which the silver atom is also coordinated to the olefin moiety.[19] This could be observed in ^{1}H-NMR by shielding of the signals corresponding to the olefin. This acid–base ligand exchange has also been proposed as the first step in oxidative decarboxylations catalyzed by Ag(I),[20] and would explain the

Table 3 Scope of the oxidative cyclization mediated by AgOAc[a]

Entry	Substrate	Product(s)
1	 R = 4-OMe (**2a**); R = 4-Cl (**3a**); R = 3-Me (**4a**); R = 5-OMe (**5a**);	 R = 7-OMe (**2b**, 44%); R = 7-Cl (**3b**, 36%); R = 8-Me (**4b**, 65%); R = 6-OMe (**5b**, 60%);
2	 X = Cl (**6a**); X = NO_2 (**7a**);	 X = Cl (**6b**, 32%); X = NO_2 (**7b**, 0%); X = Cl (**6c**, 32%) X = NO_2 (**7c**, 65%)
3	 **8a**	 **8b** (4%) **8c** (7%)
4	 **9a**	 **9b** (50%)
5	 X = S (**10a**); X = NTs (**11a**);	 X = S (**10b**, 84%); X = NTs (**11b**, 67%);
6	 X = O (**12a**); X = S (**13a**);	 X = O **12b** (20%); X = S **13b** (47%);
7	 X = O, R_1 = H, R_2 = Ph (**14a**); X = O, R_1 = R_2 = Me (**15a**); X = NTs, R_1 = R_2 = Me (**16a**);	 **14c** (58%) X = O or NTs, R_1 = R_2 = Me decomp.
8	 X = -C(O)NHSO$_2$Ph (**17a**); X = H (**18a**);	—
9	 **19a**	 **17c** (81%)
10	 **20a**	—

[a] Reaction conditions: substrate (0.08 mmol ml^{-1}), AgOAc (3 equiv.), DMSO, 120 °C, 18 h.



Scheme 1 Test for trapping possible allyl radical intermediates.

dependency on the basicity of the silver counteranion. Once the Ag(I)-benzoate is formed, we hypothesized that under the reaction conditions Ag(I) is oxidized to one of its high oxidation states, as Ag(I) is not electrophilic enough to execute a C–H bond activation. One possibility is that Ag(I) be oxidized to Ag(II) and that **1b** be formed by a radical pathway involving allyl radicals as intermediates. Oxidative decarboxylations of acids promoted by Ag(II) are known to take place by a radical mechanism.[21] With the aim of proving the participation of allyl radicals in the reaction, we synthesized the cyclopropyl benzoic acid **21a** as a radical clock and subjected it to the reaction conditions (Scheme 1). However no reaction was observed disapproving the participation of allyl radicals as intermediates. This is in accord with the observed effect of the addition of substituents on the allyl moiety. A more substituted allyl unit would furnish a more stable allyl radical increasing the yields of the oxidative cyclization. Instead, substrates bearing substituents at the allyl moiety (**12a–16a**) were cyclized in low yields, decomposed or gave decarboxylation products. Moreover, if radicals were involved as intermediates, it would be expected that **19a** with a benzyloxy group would have cyclized in good yield. Additionally, we tried to detect the participation of Ag(II) species by EPR spectroscopy. For this, EPR spectroscopy of the reaction was carried out just before the addition of AgOAc, and after 4, 8 and 18 hours of heating. However, no absorption was detected.

Another possibility is that the compound be formed *via* a Ag(I)/Ag(III) catalytic cycle similar to the generally accepted mechanism of allylic oxidation with Pd(II).[22] Ag(III) species have been proposed as the intermediate in various organic transformations, and recently the group of Ribas has described the first example of an oxidative addition of Ag(I) to Ag(III) by a C–X bond.[23] A mechanism similar to that shown by Pd(II) could explain the inefficacy of the cyclization on **19a** and substituted allyl substrates, due to the less effective olefin coordination. By this mechanism, the decarboxylation products would be formed when the coordination to the olefin is not effective, from a Ag–benzoate by a concerted Ag–Aryl bond formation and CO_2 extrusion process.[20]

In order to gain more insights into the mechanism, we investigated the possibility that the residual oxygen present in the reaction vessel oxidizes the Ag(I) atom. With this purpose we performed the cyclization under an oxygen atmosphere (balloon). Under these conditions the yield of **1b** lowered to 50%. On the other hand in the presence of oxidants typically employed for the oxidation of Ag(I)[5,21] we also observed a decrease in the yield. Thus performing the reaction under the optimized conditions in the presence of 1 equiv. of $(NH_4)_2$-

$Ce(NO_3)_6$ the yield lowered to 10%, while in the presence of 1 equiv. of $K_2S_2O_8$ the yield lowered to 8%. A third possibility is that the oxidation might be performed by DMSO. In bibliography there are reports of oxidations of Pt and other transition metal complexes performed by a molecule of DMSO, which is reduced to SMe_2.[24] Theoretical calculations are under way in order to clarify the mechanism.

In conclusion, we have found that like other transition metal reagents, AgOAc is able to promote the oxidation of a C–H bond at an allylic position. To the best of our knowledge this is the first report on such reactivity with silver. The overall process involves the oxidative cyclization of alkenoic acids derived from salicylic acid and analogues to 4*H*-benzo[*d*][1,3]-dioxin-4-ones. The experimental results disfavour the participation of radicals or Ag(II) species in the cyclization.

Acknowledgements

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