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Silver(I)-catalyzed reaction of terminal alkynes with (diacetoxyiodo) benzene: a convenient, efficient and clean preparation of α-acetoxy ketones

Guisheng Deng [a,b,*], Jing Luo [a]

[a] College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, Hunan 410081, China
[b] Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Hunan Normal University), Ministry of Education, Changsha, Hunan 410081, China

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ABSTRACT

Silver(I)-catalyzed reaction of terminal alkynes with (diacetoxyiodo)benzene in wet acetonitrile at room temperature afforded the corresponding α-acetoxy ketones in 55–93% yields. The salient features of this reaction are the effective utilization of $PhI(OAc)_2$, high chemoselectivity, excellent yields, mild reaction conditions and the experimental simplicity. A plausible mechanism has been proposed based on the experimental results.

1. Introduction

α-Acetoxyketones are one class of useful and important synthetic intermediates.[1–7] To date many procedures have been developed to prepare these compounds, such as the anodic oxidation of enol acetates in acetic acid,[6] acetolysis of epoxides in the cholestane series,[7] the acetolysis of α-bromo ketones,[8] the acetylation of α-hydroxyl ketones,[9] the metal-catalyzed O–H insertion reaction of α-diazo ketones with carboxylic acids,[10] the conjugate addition of acyloxy groups to alkynylphenyliodonium tetrafluoroborates under both basic and acidic conditions,[11] the oxidation of trimethylsilyl enol ethers with lead tetraacetate[12] and the oxidation of ketones with lead tetraacetate[6,13] or with manganese(III) acetate in acetic acid.[14] Some other oxidants were also used in the transformation of ketones into α-acetoxy ketones.[15,16] However, they suffered from multi-steps, the low yields or environmental problem.

Recently, one-pot preparation of α-acetoxy ketones from terminal alkynes, has been paid many attention,[17] such as the mercury(II) acetate-catalyzed one-pot oxidation of terminal alkynes by sodium perborate in acetic acid.[18] In particular, (diacetoxyiodo) benzene (DIB)-induced oxidation of terminal alkynes in different acids (e.g., H_2SO_4,[19] HOAc[20,21]) has been confirmed to be an effective procedure for synthesis of α-acetoxy ketones. However, despite these efforts, the drawback of the above-mentioned approaches is low chemoselectivity,[19] higher reaction temperature,[20,21] excessive usage of $PhI(OAc)_2$,[21] lower yield[19] or the limitation on use of only aliphatic terminal alkynes as substrates.[18] Therefore, research towards exploring new activators for the hypervalent iodine(III)-mediated direct transformation of terminal alkynes (particularly, terminal aryl alkynes) to the corresponding α-acetoxy ketones is still very necessary and exigent.

In view of the catalytic role[22] of the silver(I) ion in the addition of various reagents across carbon–carbon multiple bonds and our interest,[23] we envisioned that a suitable silver(I) ion could improve the reaction of terminal alkynes with $PhI(OAc)_2$ via interaction of the carbon–carbon triple bond and the metal ion to provide a more efficient access to α-acetoxy ketones.

2. Results and discussion

In the initial stages of this investigation, phenylacetylene was selected as the standard substrate to establish an effective reaction system based on the above-mentioned protocol. The mixture of phenylacetylene **1a** (1 equiv) and $PhI(OAc)_2$ (1 equiv) in wet

* Corresponding author. Tel.: +86 731 8887 2531; e-mail addresses: gsdeng@hunnu.edu.cn, g_s_deng@sina.com (G. Deng).

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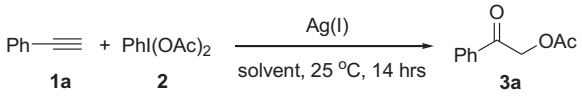
acetonitrile was treated with or without 10 mol % silver acetate at 25 °C for 14 h. When no silver(I) compounds were used, the desired product **3a** was obtained only in 9% yield (Table 1, entry 1). Phenylacetylene **1a** was completely converted to α-acetoxy acetophenone **3a** in the presence of 10 mol % CH_3COOAg in high isolated yield (up to 93%) without by-product (Table 1, entry 2). A complicated reaction was observed when CF_3COOAg, CF_3SO_3Ag or AgF were utilized as catalyst. In the cases, the desired product **3a** was obtained in low yield (Table 1, entries 3–5). When AgCl, AgBr, AgI, Ag_2O and Ag_2SO_4 were employed, the heterogeneous reactions cleanly afforded product **3a** in 76%, 79%, 73%, 80% and 75% yields, respectively (Table 1, entries 6–10). Among the investigated silver(I) compounds, the best result was obtained from silver acetate.

A survey of solvents indicated that the reaction is sensitive to the reaction medium. For example, silver acetate-catalyzed reaction in wet THF afforded the desired product **3a** in poor yield because of the formation of unknown by-product (Table 1, entry 11). Moderate yields were obtained when wet dioxane, CH_2Cl_2, $CHCl_3$, benzene, toluene and MeOH were chosen as solvents (Table 1, entries 12–17). The yield dramatically decreased when the reaction was carried out in dry acetonitrile (Table 1, entry 18). The result strongly suggests that a small amount of water is extremely important but is not necessary to this transformation. Wet acetonitrile proved to be optimal for the reaction (Table 1, entry 2).

It is well-known that more catalysts can accelerate reactions. Thus, we began to investigate the effect of the amount of silver acetate on the reaction to determine an optimal loading of the catalyst. Utilization of 1 mol %, 5 mol % and 10 mol % silver acetate in wet CH_3CN gave **3a** in 52%, 82% and 93% yields, respectively (Table 1, entries 19–20 and 2). As expected, the yields were accelerated. However, in contrast with the results anticipated, the yields were lower than that obtained in 10 mol % AgOAc-catalyzed system when using 20 mol %, 30 mol %, 50 mol % and 100 mol % AgOAc (Table 1, entries 21–24). Obviously, the best result was obtained in the presence of 10 mol % silver acetate. Only 1 equiv of $PhI(OAc)_2$ was required to accomplish the reaction.

Table 1
Optimization of reaction conditions[a]



1a 2 3a

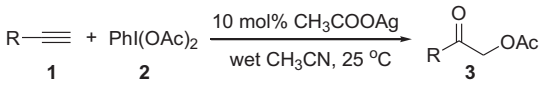
Entry	Ag(I)	The amount of catalyst (mol %)	Solvent[b]	Yield[c] (%)
1	None	—	CH_3CN	9
2	CH_3COOAg	10	CH_3CN	93
3	CF_3COOAg	10	CH_3CN	44[d]
4	CF_3SO_3Ag	10	CH_3CN	38[d]
5	AgF	10	CH_3CN	52[d]
6	AgCl	10	CH_3CN	76
7	AgBr	10	CH_3CN	79
8	AgI	10	CH_3CN	73
9	Ag_2O	10	CH_3CN	80
10	Ag_2SO_4	10	CH_3CN	75
11	CH_3COOAg	10	THF	10[d]
12	CH_3COOAg	10	Dioxane	60
13	CH_3COOAg	10	CH_2Cl_2	62
14	CH_3COOAg	10	$CHCl_3$	59
15	CH_3COOAg	10	Benzene	52
16	CH_3COOAg	10	Toluene	64
17	CH_3COOAg	10	MeOH	55
18	CH_3COOAg	10	Dry CH_3CN	35[e]
19	CH_3COOAg	100	CH_3CN	25
20	CH_3COOAg	50	CH_3CN	43
21	CH_3COOAg	30	CH_3CN	51
22	CH_3COOAg	20	CH_3CN	60
23	CH_3COOAg	5	CH_3CN	82
24	CH_3COOAg	1	CH_3CN	52

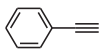
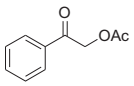
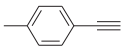
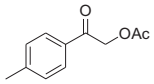
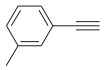
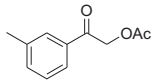
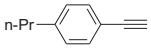
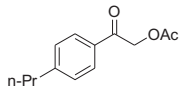
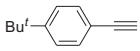
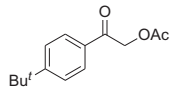
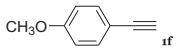
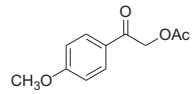
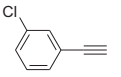
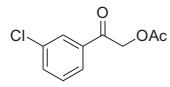
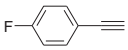
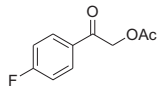
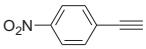
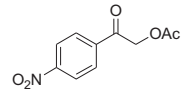
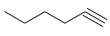
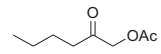
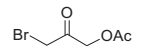
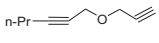
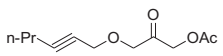
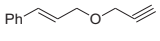
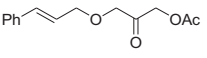
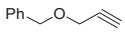
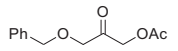
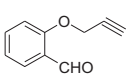
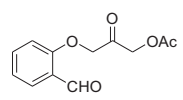
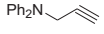
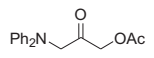
[a] All reactions were performed by using phenylacetylene (1 mmol) and $PhI(OAc)_2$ (1 mmol) in solvent (10 ml) at 25 °C for 14 h.
[b] Reaction was carried out in the solvent containing 1% water except dry solvent.
[c] Isolated yields.
[d] Unknown by-product was formed.
[e] The reaction worked under anhydrous conditions.

Under these optimized conditions, the reaction of various alkynes with $PhI(OAc)_2$ afforded expected products **3**. These results were summarized in Table 2. The use of phenylacetylene as a substrate gave α-acetoxy acetophenone in 93% yield (Table 2, entry 1). When aryl acetylenes bearing electron-rich groups, such as alkyl and alkoxy at the 3 or 4-position of benzene ring were employed as substrates, a longer time was needed for complete reaction (Table 2, entries 2–6). When the groups were changed to electron-deficient groups, such as halo and nitro at the 2 or 4-position of benzene ring, the reaction gave rise to the corresponding product **3** in excellent yields in relatively short reaction time (Table 2, entries 7–9). The reaction of aliphatic terminal alkynes, such as 1-hexyne also afforded desired product **3j** in 55% isolated yield and 2-oxohexane-1,1-diyl diacetate as by-product in 18% isolated yield (Table 2, entry 10), however, the reactivity is lower than that of phenylacetylene and the aryl alkynes with electron-deficient groups at benzene ring. Additionally, a variety of 1-propyne derivatives, such as 3-bromo-1-propyne and propynyl ether or amine, were transformed to the corresponding products in moderate to good yields (Table 2, entries 11–16). In addition, the compound **1q** with two terminal acetylenic bonds is also a suitable substrate. $PhI(OAc)_2$ (2 equiv) reacted with the two terminal triple bonds, yielding α,α′-diacetoxy diketone **3q** as unique product without α-acetoxy ketone **4** with one triple bond intact (Table 2, entry 17). Obviously, the result is different from that reported in literature.[21] A variety of terminal alkynes were cleanly converted to the corresponding α-acetoxy ketones without the formation of by-product except *p*-methoxy phenylacetylene **1f** and 1-hexyne **1j** (Table 2, entries 6 and 10). However, 1-phenyl-1-butyne **1r** failed to afford the corresponding product (Table 2, entry 18). Moreover, the reaction showed tolerance towards the internal carbon–carbon triple or double bond and aldehyde group (Table 2, entries 12, 13 and 15).

It is generally accepted that the synthesis of α-acetoxy ketones proceeds through a Michael-type addition of a nucleophile to the electron-deficient β-carbons of the alkynyliodonium salts **6**, which are produced by the reaction of terminal alkynes with $PhI(OAc)_2$.[11,21,24] If so, both an acetate anion and water should be considered as possible nucleophiles in this reaction. The reaction of 2-propyn-1-ol **1s** provided 2-oxopropane-1,3-diyl diacetate **3s** as a unique product without the expected 3-hydroxy-2-oxopropyl acetate **3s-OH** (Table 2, entry 19), which should be produced by a Michael-type addition of water to the corresponding alkynyliodonium salts **6s** via intermediate **8s-OH** (Scheme 1, Eq. 1).[11,21,24] The transformation of **3s-OH** into **3s** has been excluded because acetylation of hydroxy groups did not take place by the reaction of **3s-OH** with 1 equiv of HOAc under these conditions (Scheme 1, Eq. 2). This indicates that the reaction do not involve the formation of **3s-OH** via intermediate **8s-OH**. More importantly, in the absence of water the reaction of 2-propyn-1-ol **1s** gave **3s** in similar yield (79%) (Scheme 1, Eq. 3) albeit longer reaction time was required comparing with the reaction in wet CH_3CN (Table 2, entry 19). Therefore, there is obvious evidence against the addition of water as a nucleophile in this reaction. To explain the transformation of the hydroxy group of **1s** to an acetoxy group under these conditions, we should consider a reaction process involving a reactive intermediate that can undergo the acetylation of the hydroxy group. We hereby propose an interpretation of a key intermediate, namely, (β-acetoxyviny1)phenyliodonium acetates **8s**,[11] which may undergo an intramolecular 1,4-shift of the acetyl group via a five-membered transition state, shown by the arrow (Scheme 1, Eq. 4). Perhaps the intermediate **8s** is produced by Michael-type

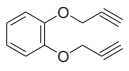
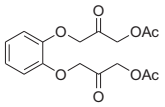
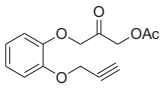
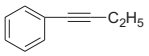
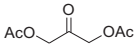
Table 2
Substrate scope of the $PhI(OAc)_2$-mediated reaction of alkynes[a]



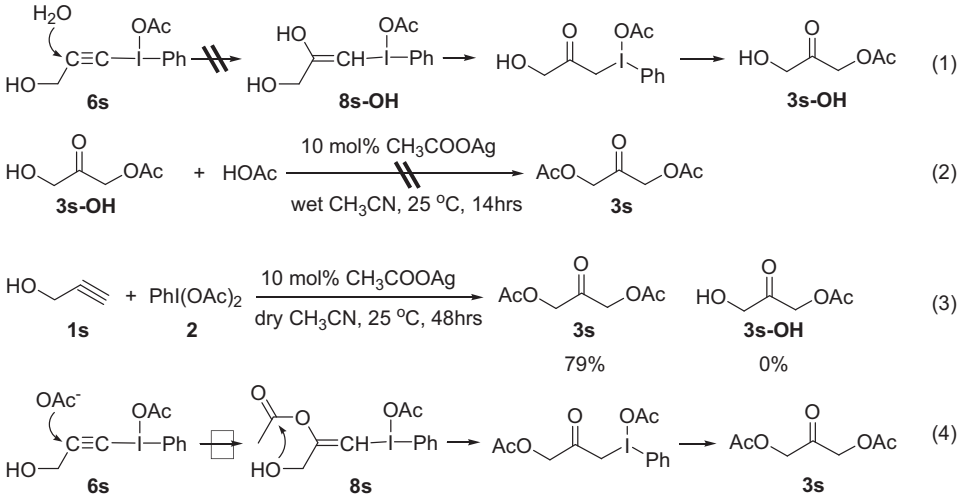
Entry	Substrate	React. time (h)	Product	Yield[b] (%)
1	 **1a**	14	 **3a**	93
2	 **1b**	18	 **3b**	87
3	 **1c**	18	 **3c**	85
4	 **1d**	20	 **3d**	83
5	 **1e**	20	 **3e**	82
6	 **1f**	18	 **3f**	72[c]
7	 **1g**	13	 **3g**	85
8	 **1h**	12	 **3h**	92
9	 **1i**	12	 **3i**	86
10	 **1j**	15	 **3j**	55[d]
11	 **1k**	14	 **3k**	86
12	 **1l**	14	 **3l**	82
13	 **1m**	18	 **3m**	75
14	 **1n**	14	 **3n**	87
15	 **1o**	20	 **3o**	60
16	 **1p**	18	 **3p**	64

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate	React. time (h)	Product	Yield[b] (%)
17	 **1q**	26	 **3q**  **4**	57 (**3q**/**4**=100:0)[e]
18	 **1r**	48	—	—[f]
19	 **1s**	14	 **3s**	83

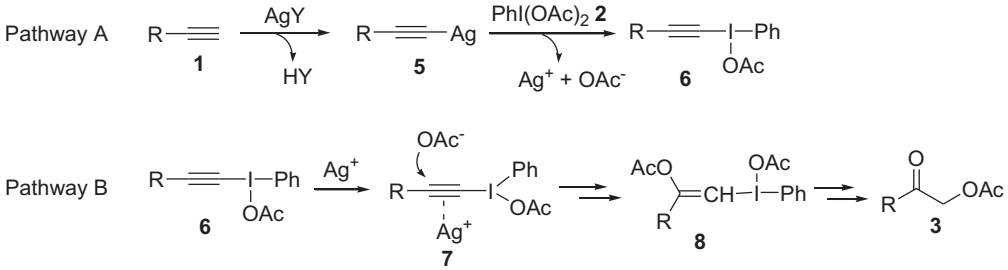
[a] Reaction conditions: alkynes (1 mmol), $PhI(OAc)_2$ (1 mmol), CH_3COOAg (0.1 mmol), CH_3CN (10 ml).
[b] Isolated yield.
[c] A small amount of unknown by-product was formed.
[d] A small amount of 2-oxohexane-1,1-diyl diacetate was produced.
[e] $PhI(OAc)_2$ (2 mmol).
[f] No reaction.



Scheme 1. A hypothesis for the transformation of the hydroxy group of **1s** to an acetoxy group.

addition of an acetate anion to the alkynyliodonium salts **6s** according to the literature (Scheme 1, Eq. 4).[11,21,24] If so, what is the role of silver(I) in the reaction?

As outlined in Scheme 2, there are two alternative pathways that Ag^+ promotes the reaction of the terminal alkynes with $PhI(OAc)_2$. In pathway A, maybe in situ-generated alkynyl silver(I) **5** from terminal alkynes **1**[25] facilitates the formation of alkynyliodonium salts **6**. In pathway B, the formation of complex **7** of Ag^+ with the carbon–carbon multiple bond of alkynyliodonium salts **6** possibly increases its electron-deficient nature to accelerate the



Scheme 2. A hypothesis for Ag^+-catalyzed reaction of terminal alkynes with $PhI(OAc)_2$.

conjugate addition of acetate anion towards the alkynyliodonium salts resulting in the formation of key intermediates **8**.

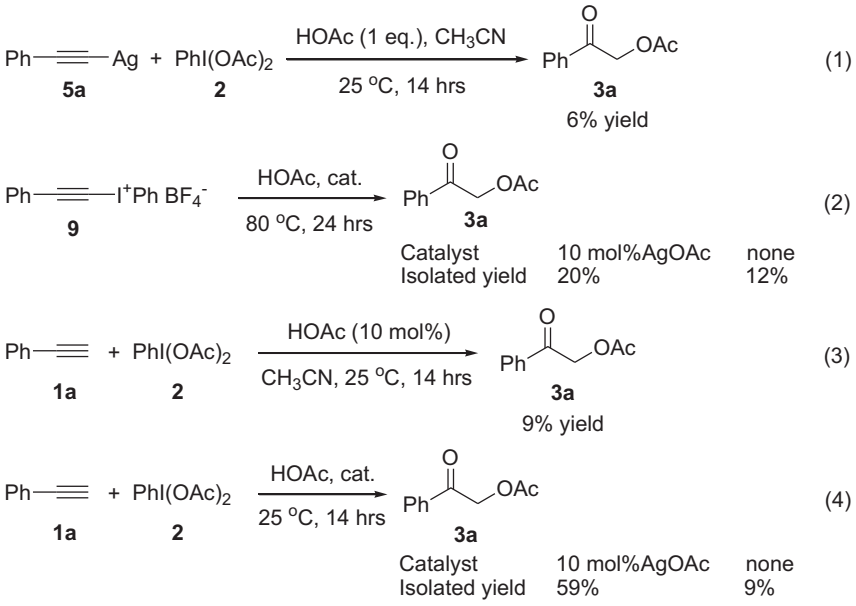
To test the hypothesis, control experiments have been accomplished. Utilization of pure phenylethynyl silver(I) **5a** in the reaction with $PhI(OAc)_2$ gave **3a** in only 6% yield (Scheme 3, Eq. 1). Considering that 1 equiv of acetate acid was formed in the transformation of phenylacetylene **1a** into the corresponding alkynyl silver(I),[25] 1 equiv of acetate acid was added to the heterogeneous reaction of phenylethynyl silver(I) **5a** with $PhI(OAc)_2$ to achieve a consistent condition. The result is similar to that in absence of silver(I) (Table 1, entry 1). Therefore, the alkynyl silver(I) does not play a role in the silver(I)-mediated reaction of terminal alkynes with $PhI(OAc)_2$ although alkynyl silver(I) is indeed generated in situ. The conjugate addition of HOAc towards phenylethynylphenyliodonium tetrafluoroborate **9**[26] in the presence or absence of 10 mol % AgOAc afforded **3a** in 20% and 12%[11] yields, respectively (Scheme 3, Eq. 2). Obviously, Ag^+ does not activate the carbon–carbon multiple bond of alkynyliodonium salts **6**. The control experiment results strongly suggest that both alkynyl silver(I) **5** and alkynyliodonium salt **6** are not key intermediates in the reaction with silver(I) activation. In contrast, alkynyl silver(I) **5** does not favour the formation of product **3** probably due to its low solubility and poor reactivity in wet CH_3CN (Table 1, entries 19–22).

Acetic acid seems to be able to facilitate the process according to literature.[21] In order to prove that the role of silver(I) or acetic acid is the key part for this system, the reaction with 10 mol % acetic acid activation was carried out (Scheme 3, Eq. 3). The yield is similar to that in the case without acetic acid activation (Table 1, entry 1). Even the use of acetic acid as solvent gave **3a** in only 9% yield.[21] When the reaction was activated with another 10 mol % AgOAc, the yield obviously increases up to 59% (Scheme 3, Eq. 4), but is apparently lower than that in the standard condition (Table 2, entry 1). These results indicate not only that silver(I) instead of acetic acid plays an important role in activation but that acetic acid is not the best reaction solvent.[21]

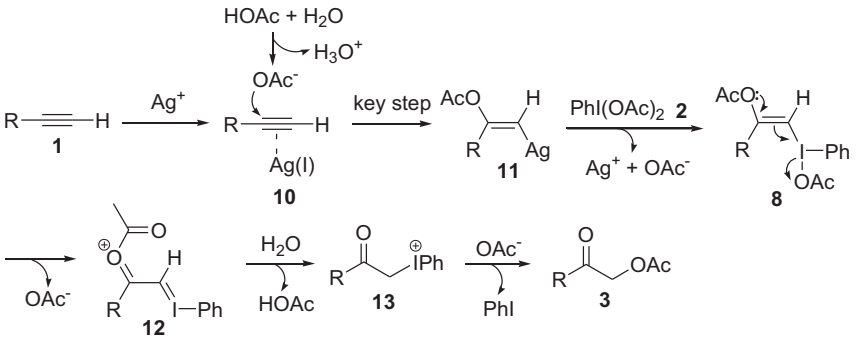
In the early time, Negishi, et al. found that the Ag(I)-catalyzed cyclization of (*Z*)-2-en-4-ynoic acids gave (*Z*)-5-alkylidenefuran-2(5*H*)-ones.[22a] Cyclic carbonates have also been synthesized using this type of reaction.[22b] Recently, Yamada, et al. reported that silver(I) promoted the incorporation of CO_2 into *o*-alkynylanilines to afford the corresponding benzoxazine-2-ones bearing *Z exo*-olefin.[22c] In these reaction sequences, the lactonization at the Ag(I)-activated C–C triple bond leading to the formation of β-acetoxyvinyl silver intermediates[22a] has been suggested as a key step. On the basis of the mechanism for above-mentioned silver(I)-promoted lactonization[22] and these observations made by us and the others,[11,21,24,27,28] a plausible mechanism of the silver(I)-catalyzed reaction involving (β-acetoxyviny1) phenyliodonium acetates **8** is proposed as shown in Scheme 4. We believe that the reaction starts from Ag(I)-activated alkynes **10**. Based on *anti*-addition rule,[11,29] the addition of trace amount acetate anion in available commercial source to the complexes **10** followed by the reaction with $PhI(OAc)_2$ gives the (β-acetoxyvinyl) iodonium **8**[24a] and 1 equiv of acetate anion via β-acetoxyvinyl silver intermediates **11**[22a] and regenerates silver ion catalyst. The acetate anion elimination of intermediates **8** yields iodonium ylides **12**. Hydrolysis of the ylides **12** by water gives alkyliodonium salts **13** and HOAc. Therefore, use of various silver(I) compounds in the reaction affords total 2 equiv of acetate anion, which again participates in subsequent reaction as nucleophile. Whereafter, the substitution of the phenyliodonium group of the salts **13** with acetate anion affords α-acetoxy ketones **3**.[11,24]

The reaction process outlined in Scheme 4 addresses the role of silver(I) and water in the sequential transformations: namely, silver(I)-activated carbon–carbon triple bond of the terminal alkynes **1** possesses higher electron-deficient nature than that of the corresponding alkynes **1**, tremendously promoting an intermolecular addition of acetate anion to the carbon–carbon triple bond; ionization of acetic acid in water yields acetate anion, which is stronger nucleophile than its conjugate acid.[11,21] In addition, hydrolysis of the ylides **12** proceeds in the medium containing water.[11]

In conclusion, we have demonstrated the silver(I)-catalyzed reaction of terminal alkynes with $PhI(OAc)_2$ for first time, and



Scheme 3. Control experiments.



Scheme 4. A plausible mechanism of the silver(I)-catalyzed reaction.

developed an efficient protocol for the preparation of α-acetoxy ketones starting from terminal alkynes in good to excellent yields. Irrespective of the precise mechanism of the reaction, however, this is an important alternative to existing approaches to synthesis of α-acetoxy ketones starting from terminal alkynes (particularly, terminal aryl alkynes) in view of the experimental simplicity, the mildness of the reaction conditions, high chemoselectivity, efficient use of $PhI(OAc)_2$ and excellent yields.

3. Experimental

3.1. General procedure

Solvents containing 1% water were used. Infrared (IR) spectra were recorded on a Nicolet Nexus TT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance-500 Spectrometer in $CDCl_3$ solution using tetramethylsilane as an internal standard. MS (FAB) and HRMS spectra were recorded on Waters ZQ2000 and Bruker APEX IV, respectively. For thin layer chromatography (TLC) analysis throughout this work, Merck 25 TLC aluminium sheets (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel ZCX-α (300–400 mesh).

3.2. General procedure for preparation of α-acetoxy ketones 3 starting from terminal alkynes 1

To a mixture of $PhI(OAc)_2$ (1 mmol, 322 mg) and CH_3COOAg (0.1 mmol, 17 mg) in CH_3CN (10 ml) was added alkyne (1 mmol). The mixture was stirred at room temperature. When $PhI(OAc)_2$ was completely disappeared by TLC analysis, the mixture was concentrated in vacuum. The residue was purified by column chromatography on silica gel with EtOAc/petroleum ether 6:1 as eluent.

*3.2.1. 2-Oxo-2-phenylethyl acetate (**3a**).*[21] ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.93–7.91 (m, 2H), 7.61 (tt, *J*=7.5, 1.0 Hz, 1H), 7.49 (t, *J*=7.5 Hz, 2H), 5.35 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 192.19, 170.47, 134.20, 133.92, 128.89, 127.77, 66.04, 20.59. IR (KBr): 3423, 2917, 2855, 2357, 1751, 1696, 1380, 1219, 1046, 687 cm^{-1}. MS (EI) 192 (M^+), 105 (100), 91, 77, 65, 51, 43.

*3.2.2. 2-Oxo-2-(p-tolyl)ethyl acetate (**3b**).*[21] ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.81 (d, *J*=7.0 Hz, 2H), 7.27 (d, *J*=7.0 Hz, 2H), 5.30 (s, 2H), 2.40 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 191.62, 170.21, 144.68, 131.60, 129.37, 127.70, 65.82, 21.56, 20.40. IR (KBr): 2957, 2922, 1748, 1698, 1602, 1369, 1225, 1085, 964, 808, 777, 603, 559 cm^{-1}. MS (EI) 192 (M^+), 119 (100), 91, 85, 65, 58, 43.

*3.2.3. 2-Oxo-2-(m-tolyl)ethyl acetate (**3c**).* ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.72 (s, 1H), 7.69 (d, *J*=7.5 Hz, 1H), 7.42–7.36 (m, 1H), 7.34 (d, *J*=7.5 Hz, 1H), 5.32 (s, 2H), 2.40 (s, 3H), 2.21 (s, 3H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 192.26, 170.35, 138.65, 134.55, 134.15, 128.61, 128.16, 124.82, 65.97, 21.20, 20.44. IR (KBr): 2851, 2730, 1756, 1590, 1366, 1221, 1042, 777, 694, 628, 541 cm^{-1}. MS (EI) 192 (M^+), 150, 119 (100), 105, 91, 77, 43. HRMS calcd for [$C_{11}H_{13}O_3$+H]: 193.0865, found: 193.0862.

*3.2.4. 2-Oxo-2-(4-propylphenyl)ethyl acetate (**3d**).* ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.82 (d, *J*=7.0 Hz, 2H), 7.27 (d, *J*=7.0 Hz, 2H), 5.31 (s, 2H), 2.63 (t, *J*=7.5 Hz, 2H), 2.21 (s, 3H), 1.69–1.61 (m, 2H), 0.93 (t, *J*=7.5 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 191.60, 170.20, 149.25, 131.77, 128.73, 127.67, 65.79, 37.85, 23.94, 20.33, 13.50. IR (KBr): 2961, 2930, 2861, 1755, 1700, 1606, 1416, 1375, 1224, 1090, 965, 813, 607, 569 cm^{-1}. MS (EI) 220 (M^+), 147, 139, 119, 91, 58, 43 (100). HRMS calcd for [$C_{13}H_{17}O_3$+H]: 221.1178, found: 221.1180.

*3.2.5. 2-(4-(tert-Butyl)phenyl)-2-oxoethyl acetate (**3e**).* ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.85 (d, *J*=8.0 Hz, 2H), 7.49 (d, *J*=8.0 Hz, 2H), 5.32 (s, 2H), 2.21 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 191.63, 170.24, 157.57, 131.51, 127.58, 125.65, 65.84, 35.05, 30.86, 20.40. IR (KBr): 2963, 2867, 1752, 1702, 1599, 1222, 1089, 981, 832, 724, 645, 575 cm^{-1}. MS (EI) 234 (M^+), 161, 139, 119, 91, 75, 58, 43 (100). HRMS calcd for [$C_{14}H_{19}O_3$+H]: 235.1334, found: 235.1339.

*3.2.6. 2-(4-Methoxyphenyl)-2-oxoethyl acetate (**3f**).*[30] ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.88 (d, *J*=9.0 Hz, 2H), 7.94 (d, *J*=9.0 Hz, 2H), 5.29 (s, 2H), 3.86 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 190.53, 170.36, 163.94, 129.93, 127.10, 113.93, 65.65, 55.39, 20.45. IR (KBr): 2937, 2840, 1755, 1689, 1597, 1441, 1214, 1167, 1090, 967, 831, 775, 608, 563 cm^{-1}. MS (EI) 208 (M^+), 135 (100), 107, 92, 77, 65, 58, 43.

*3.2.7. 2-(3-Chlorophenyl)-2-oxoethyl acetate (**3g**).*[30] ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.86 (t, *J*=2.0 Hz, 1H), 7.77 (d, *J*=8.0 Hz, 1H), 7.57–7.44 (m, 1H), 7.42 (t, *J*=8.0 Hz, 1H), 5.29 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 191.00, 170.15, 135.51, 135.02, 133.62, 130.07, 127.69, 125.65, 65.77, 20.29. IR (KBr): 3070, 2925, 1755, 1730, 1580, 1425, 1370, 1211, 1083, 848, 785, 739, 679, 599 cm^{-1}. MS (EI) 212 (M^+), 139, 111, 85, 71, 57, 43 (100).

*3.2.8. 2-(4-Fluorophenyl)-2-oxoethyl acetate (**3h**).*[30] ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.96–7.93 (m, 2H), 7.15 (t, *J*=7.5 Hz, 2H), 5.30 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 191.57, 170.20, 166.91, 164.87, 130.49, 130.46, 130.34, 130.27, 115.96, 115.78, 65.65, 20.25. IR (KBr): 3390, 2921, 2801, 2606, 2428, 2063, 1926, 844, 736, 566, 492 cm^{-1}. MS (EI) 196 (M^+), 123 (100), 95, 75, 58, 43.

*3.2.9. 2-(4-Nitrophenyl)-2-oxoethyl acetate (**3i**).*[31] ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 8.35 (d, *J*=7.5 Hz, 2H), 8.10 (d, *J*=7.5 Hz, 2H), 5.34 (s, 2H), 3.86 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$,

ppm) δ 191.00, 170.24, 150.69, 138.60, 128.88, 124.04, 66.02, 20.37. IR (KBr): 2946, 2855, 1752, 1704, 1525, 1369, 1348, 1218, 974, 855, 810, 747, 686 cm^{-1}. MS (EI) 223 (M^+), 150, 104, 92, 78, 58, 43 (100).

*3.2.10. 2-Oxohexyl acetate (**3j**).*[21] ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 4.66 (s, 2H), 2.42 (d, *J*=7 Hz, 2H), 2.17 (s, 3H), δ 1.63–1.57 (m, 2H), 1.36–1.32 (m, 2H), 0.91 (t, *J*=7 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 203.91, 170.15, 67.83, 38.35, 25.23, 22.11, 20.33, 13.64. IR (KBr): 2930, 2845, 1744, 1378, 1226, 1049, 857, 600 cm^{-1}.

*3.2.11. 3-Bromo-2-oxopropyl acetate (**3k**).* ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 4.91 (s, 2H), 3.95 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 195.76, 170.10, 66.01, 30.36, 20.34. IR (KBr): 2930, 2843, 1744, 1371, 1226, 1047, 857, 703, 612 cm^{-1}. MS (EI) 196 (M+2), 194 (M^+), 150, 134, 120, 102, 73, 43 (100). HRMS calcd for [$C_5H_8BrO_3$+H]: 194.9657, found: 194.9651.

*3.2.12. 3-(Hex-2-yn-1-yloxy)-2-oxopropyl acetate (**3l**).* ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 4.87 (s, 2H), 4.21 (t, *J*=1.0 Hz, 2H), 4.20 (s, 2H), 2.18–2.14 (m, 2H), 2.13 (s, 3H), 1.52–1.47 (m, 3H), 0.94 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 201.89, 170.14, 88.65, 74.51, 66.81, 59.33, 21.80, 20.56, 20.33, 13.35. IR (KBr): 2963, 2872, 1740, 1421, 1379, 1226, 1097, 1072, 604 cm^{-1}. MS (EI) 212 (M^+), 169, 141, 99, 79, 53, 43 (100). HRMS calcd for [$C_{16}H_{17}O_4$+H]: 213.1127, found: 213.1120.

*3.2.13. (E)-3-(Cinnamyloxy)-2-oxopropyl acetate (**3m**).*[21] ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.40–7.39 (m, 2H), 7.34–7.31 (m, 2H), 7.27–7.24 (m, 1H), 6.62 (d, *J*=16 Hz, 1H), 6.26 (dt, *J*=16, 6 Hz, 1H), 4.90 (s, 2H), 4.22 (d, *J*=6 Hz, 2H), 4.17 (s, 2H), 2.16 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 202.04, 170.19, 136.11, 133.75, 128.55, 127.96, 126.50, 124.36, 73.52, 72.21 66.76, 20.35. IR (KBr): 3433, 2937, 2860, 1738, 1640, 1400, 1117, 1060, 675, 558 cm^{-1}. MS (EI) 249 M+1$^+$, 207, 191, 177, 133, 131, 117 (100), 115, 105, 91, 79, 65, 43.

*3.2.14. 3-(Benzyloxy)-2-oxopropyl acetate (**3n**).*[32] ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.38–7.33 (m, 5H), 4.90 (s, 2H), 4.59 (s, 2H), 4.14 (s, 2H), 2.16 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 201.96, 170.24, 136.70, 128.60, 128.21, 127.90, 73.76, 73.71, 66.83, 20.41. IR (KBr): 2930, 2863, 1748, 1375, 1230, 1110, 1090, 745, 695, 612 cm^{-1}. MS (EI) 222 (M^+), 161, 148, 115, 77, 55, 43 (100).

*3.2.15. 3-(2-Formylphenoxy)-2-oxopropyl acetate (**3o**).* ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 10.51 (s, 1H), 7.88 (dd, *J*=8, 2 Hz, 1H), 7.58 (dt, *J*=8, 2 Hz, 1H), 7.14 (t, *J*=8 Hz, 1H), 6.87 (d, *J*=8 Hz, 1H), 5.01 (s, 2H), 4.82 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 199.37, 188.88, 170.25, 159.23, 136.00, 129.68, 125.13, 122.21, 112.31, 71.71, 66.70, 20.33. IR (KBr): 3444, 2919, 2854, 1738, 1682, 1596, 1471, 1384, 1233, 1058, 753 cm^{-1}. MS (EI) 236 (M^+), 218, 194, 176, 163, 145, 121, 118, 107, 92, 77, 73, 63, 43 (100). HRMS calcd for [$C_{12}H_{13}O_5$+H]: 237.0763, found: 237.0767.

*3.2.16. 3-(Diphenylamino)-2-oxopropyl acetate (**3p**).* ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28–7.24 (m, 4H), 7.02–6.97 (m, 6H), 4.82 (s, 2H), 4.54 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 203.04, 170.26, 147.27, 129.56, 122.37, 120.47, 67.31, 60.46, 20.35. IR (KBr): 3460, 3050, 2917, 1748, 1590, 1490, 1362, 1229, 1051, 752, 690, 594, 507 cm^{-1}. MS (EI) 283 (M^+), 182 (100), 104, 77, 51, 43. HRMS calcd for [$C_{17}H_{18}NO_3$+H]: 284.1287, found: 284.1286.

*3.2.17. 3,3′-(1,2-Phenylenebis(oxy))bis(2-oxopropane-3,1-diyl) diacetate (**3q**).* Yield: 57%; ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 6.94–6.92 (m, 2H), 6.83–6.81 (m, 2H), 4.97 (s, 4H), 4.68 (s, 4H), 2.12 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 200.58, 170.31, 147.59, 122.89, 114.87, 72.81, 66.80, 20.41. IR (KBr): 2954, 2909, 1743, 1503, 1420, 1382, 1233, 1018, 748 cm^{-1}. MS (EI) 338 (M^+), 224, 164, 164, 147, 135, 115, 81, 61, 43 (100). HRMS calcd for [$C_{16}H_{18}O_8$+H]: 339.1080, found: 339.1076.

*3.2.18. 2-Oxopropane-1,3-diyl diacetate (**3s**).*[33] ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 4.73 (s, 4H), 2.14 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm) δ 197.92, 170.04, 66.19, 20.25. IR (KBr): 3440, 2925, 2855, 1743, 1640, 1441, 1378, 1225, 1051, 874, 599 cm^{-1}. MS (EI) 174 (M^+), 116, 101, 58, 43 (100).

3.3. Reaction of phenylethynyl silver 5a with PhI(OAc)$_2$

To a mixture of $PhI(OAc)_2$ (1 mmol, 322 mg), CH_3COOAg (0.1 mmol, 17 mg), phenylethynyl silver (1 mmol, 209 mg) in CH_3CN (10 ml) was added HOAc (1 mmol, 60 mg). The mixture was stirred at room temperature for 14 h. The mixture was concentrated in vacuum. The residue was purified by column chromatography on silica gel with EtOAc/petroleum ether 6:1 as eluent to afford α-acetoxy acetophenone **3a** in 6% yield.

3.4. Reaction of phenylethynylphenyliodonium tetrafluoroborates 9 with HOAc[11]

A mixture of phenylethynylphenyliodonium tetrafluoroborates (1 mmol, 392 mg) in HOAc (2 ml) was stirred in the presence or absence of CH_3COOAg (0.1 mmol, 17 mg) at 80 °C for 24 h. The mixture was concentrated in vacuum. The residue was purified by column chromatography on silica gel with EtOAc/petroleum ether 6:1 as eluent to afford α-acetoxy acetophenone **3a** in 20% and 12% yield, respectively.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.04.122. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

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