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Catalyst-free synthesis of α-thioacrylic acids *via* cascade thiolation and 1,4-aryl migration of aryl alkynoates at room temperature†

Wei Wei, *[a,b,c] Leilei Wang,[c] Huilan Yue,*[b] Yuan-Ye Jiang [c] and Daoshan Yang [a,c]

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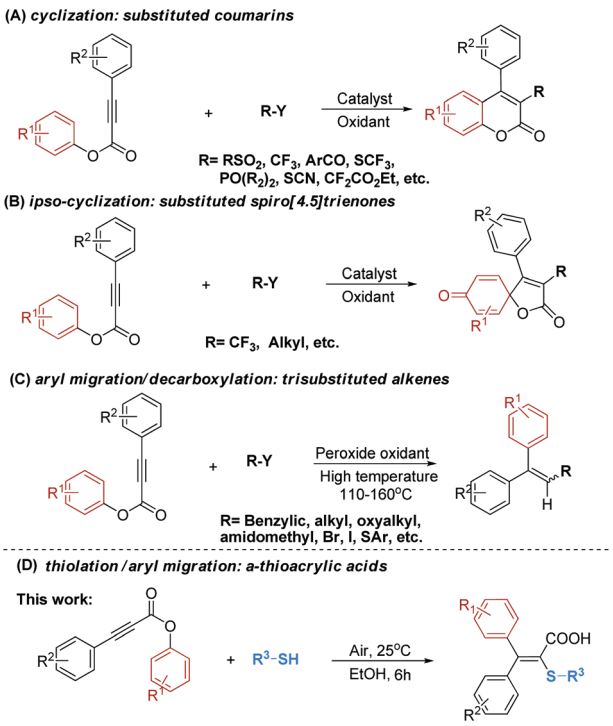
A simple and facile catalyst-free method for the construction of α-thioacrylic acids has been developed from readily-available aryl alkynoates and thiols at room temperature. Various α-thioacrylic acids could be conveniently and efficiently obtained in moderate to good yields *via* cascade thiolation and 1,4-aryl migration of aryl alkynoates in the absence of any catalyst and additive.

Introduction

Sulfur-containing compounds are present in numerous medicines,[1] agrochemicals[2] and materials.[3] Over the past few decades, the introduction of sulfur groups into organic frameworks *via* C–S bond formation has attracted considerable interest of chemists due to their extensive applications in synthetic and pharmaceutical chemistry.[4] In this field, the functionalization of alkynes with thiolating reagents represents one of the most powerful and straightforward procedures for the synthesis of organosulfur compounds owing to the ready availability and synthetic versatility of the alkyne moiety.[5,6] Nevertheless, many thiolation reactions of alkynes usually need the use of transition-metal catalysts and stoichiometric additives, or suffer from low atom-efficiency and harsh reaction conditions. Thus, the development of mild, convenient, atom-economical, and metal-free methods for thiolation of alkynes still remains a significant challenge.

Alkynoates are a kind of fascinating and valuable building block, which can be utilized for various organic transformations toward many useful compounds in organic synthesis.[7] In recent years, alkynoates as good radical receptors have been widely used for the construction of substituted heterocycles such as coumarins[8] and azaspiro[4.5]trienone derivatives[9] *via* cascade radical addition and cyclization/*ipso*-cyclization reactions (Scheme 1(A) and (B)). Through this strategy, some useful functional groups such as phosphoryl, trifluoromethyl, arylsulfonyl, acyl, trifluoromethylthio, oxyalkyl and organoselenyl groups could be successfully introduced into the heterocycle frameworks. Very recently, sequential oxidative radical addition, intramolecular 1,4-aryl migration and decarboxylation reactions of alkynoates have also been developed to con-



Scheme 1 Functionalization of alkynoates.

[a]State Key Laboratory Base of Eco-Chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, 266042, P. R. China. E-mail: weiweiqfnu@163.com
[b]Key Laboratory of Tibetan Medicine Research, Northwest Institute of Plateau Biology, Chinese Academy of Sciences and Qinghai Provincial Key Laboratory of Tibetan Medicine Research, Qinghai 810008, China. E-mail: hlyue@nwipb.cas.cn
[c]School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, China

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struct a series of trisubstituted alkenes in the presence of stoichiometric amounts of peroxide oxidants at high temperature (110–160 °C)[10] (Scheme 1(C)). Inspired by the well-developed migration/decarboxylation reactions, we envision that the addition of suitable radical species to the alkyne unit of aryl alkynoates under mild conditions would trigger an aryl migration without decarboxylation to give substituted acrylic acids, which are extremely useful compounds for the construction of biologically active materials, lubricant additives, or polymers.[11]

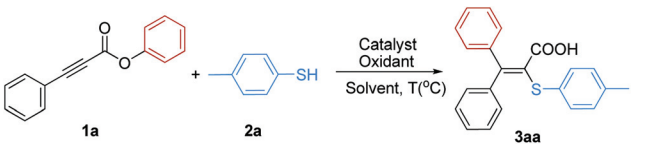
With our continued interest in the construction of sulfur-containing compounds,[12] here, we wish to report a simple and convenient method for the construction of various α-thioacrylic acids *via* cascade thiolation and 1,4-aryl migration of aryl alkynoates at room temperature in the absence of any catalyst and additive (Scheme 1(D)).[13]

Results and discussion

Initially, 3-phenylpropiolate **1a** and 4-methylbenzenethiol **2a** were selected as the model substrates to optimize conditions under air. To our delight, the desired product **3aa** could be obtained in 56% yield by using the I_2/DMSO system at room temperature (Table 1, entry 1). Furthermore, the yields were slightly improved when a series of metal catalysts such as Cu, Fe and Ag salts were employed to replace molecular iodine in this reaction system (Table 1, entries 2–6). Unexpectedly, the desired product **3aa** was still obtained in 64% yield when the model reaction was carried out in the absence of the catalyst (Table 1, entry 7). Then, the solvent effect was further investigated in the absence of the catalyst (Table 1, entries 8–17). The result showed that CH_3CN, DMF, and ethers such as DME, THF, and 1,4-dioxane gave moderate yields (Table 1, entries 8–12). A relatively lower reaction efficiency was observed when the reaction was carried out in CH_2Cl_2, DCE, toluene, or H_2O (Table 1, entries 13–16). Among the various solvents screened, EtOH was found to be the best one to give the desired product **3aa** in 74% yield (Table 1, entry 17). Next, replacement of air (O_2) with other oxidants such as TBHP, $PhI(OAc)_2$, $K_2S_2O_8$ and H_2O_2 have led to lower yields due to the generation of the disulfide byproduct (Table 1, entries 18–21). The reaction efficiency was not obviously improved when the reaction was conducted under a pure oxygen atmosphere (Table 1, entry 22). Reducing the loading of **2a** gave relatively lower yields (Table 1, entries 23 and 24). In addition, the increase of reaction temperature did not improve the reaction efficiency (Table 1, entries 25–27).

Upon optimization of the reaction conditions, the substrate scope for the present transformation was surveyed. As shown in Table 2, the reactions of 3-phenylpropiolate with various arylthiols containing electron-rich or electron-poor groups on the aryl rings gave the corresponding products **3aa–3an** in moderate to good yields. It was found that the substituents on the aromatic ring of thiols including methoxyl, fluoro, bromo, chloro and hydroxy could all be well tolerated, which made this protocol more useful for further structural transformation (**3ae–3am**). The reaction efficiency was not significantly affected by the steric effect, and substrates containing a methyl or chloro group in the *para*-, *meta*-, or *ortho*-position of the aryl ring were all compatible with this process (**3aa–3ac**, and **3ag–3ai**). Notably, a heterocycle arylthiol such as 2-methylfuran-3-thiol was also a suitable substrate leading to the product **3an** in 74% yield. As expected, alkyl thiols such as (4-*tert*-butylphenyl)methanethiol and butane-1-thiol were also feasible for the reactions, but lead to the corresponding products **3ao** and **3ap** in relatively low yields. Furthermore, the scope of alkynoates was explored. A series of substituted alkynoates were all suitable substrates, affording the corresponding products **3ba–3fa** in good yields. The regioselectivity of this reaction was also investigated by using the substrates with different substituted aromatic rings on the alkynyl moiety and ester group. All these examined alkynoates could work very well in this reaction to selectively produce the corresponding product **3ga–3qa** in good yields. The regioselective outcome favors an intramolecular ipsocyclization and 1,4-aryl migration process, which is consistent with the previous

Table 1 Optimization of reaction conditions[a]



Entry	Catalyst (5 mol%)	Oxidant	Solvent	Yield[b] (%)
1	I_2	Air(O_2)	DMSO	56
2	CuBr	Air(O_2)	DMSO	66
3	$CuBr_2$	Air(O_2)	DMSO	65
4	CuCl	Air(O_2)	DMSO	61
5	$FeCl_3$	Air(O_2)	DMSO	62
6	$AgNO_3$	Air(O_2)	DMSO	64
7	—	Air(O_2)	DMSO	64
8	—	Air(O_2)	CH_3CN	63
9	—	Air(O_2)	DMF	56
10	—	Air(O_2)	DME	62
11	—	Air(O_2)	1,4-Dioxane	56
12	—	Air(O_2)	THF	55
13	—	Air(O_2)	CH_2Cl_2	44
14	—	Air(O_2)	DCE	33
15	—	Air(O_2)	Toluene	42
16	—	Air(O_2)	H_2O	26
17	—	**Air(O_2)**	**EtOH**	**74**
18	—	TBHP (1 eq.)	EtOH	58
19	—	$PhI(OAc)_2$ (1 eq.)	EtOH	22
20	—	$K_2S_2O_8$ (1 eq.)	EtOH	62
21	—	H_2O_2 (1 eq.)	EtOH	53
22	—	O_2	EtOH	74
23	—	Air(O_2)	EtOH	62[c]
24	—	Air(O_2)	EtOH	70[d]
25	—	Air(O_2)	EtOH	70[e]
26	—	Air(O_2)	EtOH	71[f]
27	—	Air(O_2)	EtOH	68[g]

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), catalyst (5 mol%), oxidant (0.2 mmol), solvent (1 mL), rt, 6 h. [b] Isolated yields based on **1a**. [c] 1.2 eq. [d] 1.5 eq. [e] 40 °C. [f] 60 °C. [g] 80 °C.

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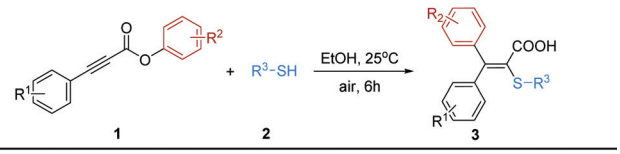
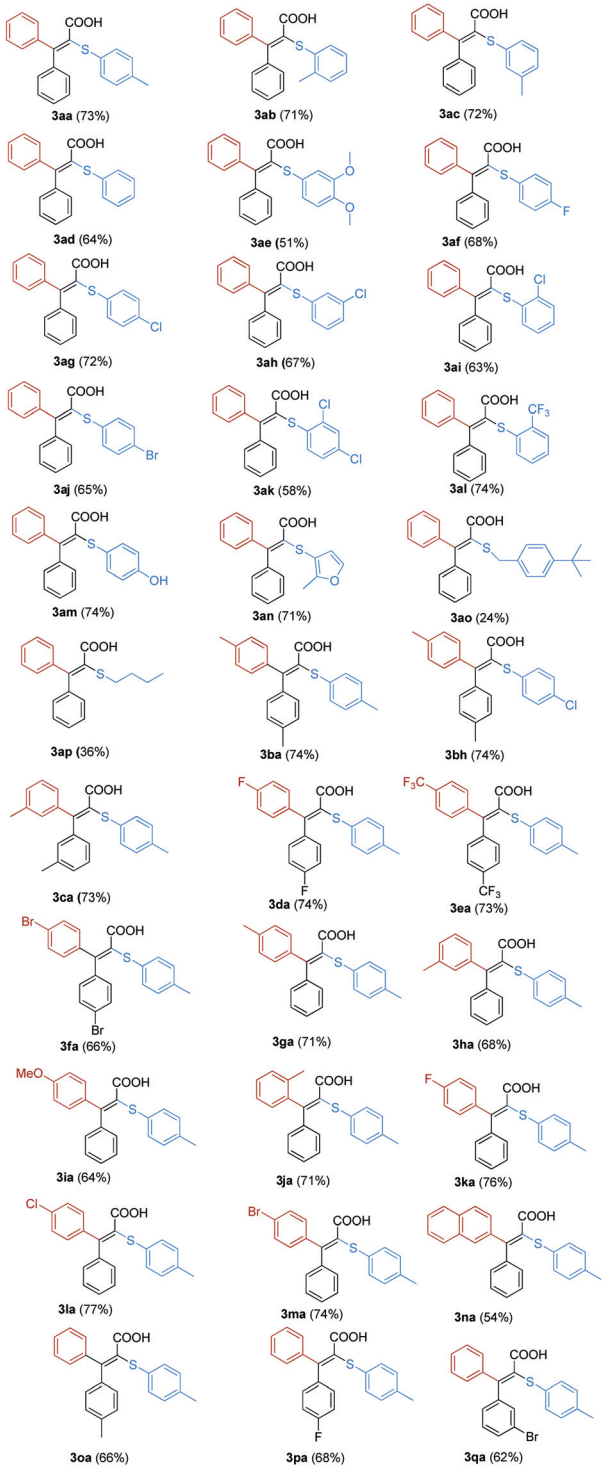
Table 2 Results of cascade thiolation and 1,4-aryl migration of aryl alkynoates leading to α-thioacrylic acids[a,b]



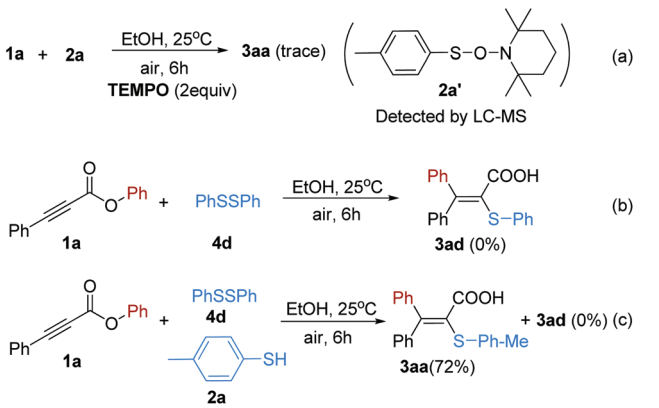


[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), EtOH (1 mL), rt, air (O_2), and 6 h. [b] Isolated yields based on **1**.

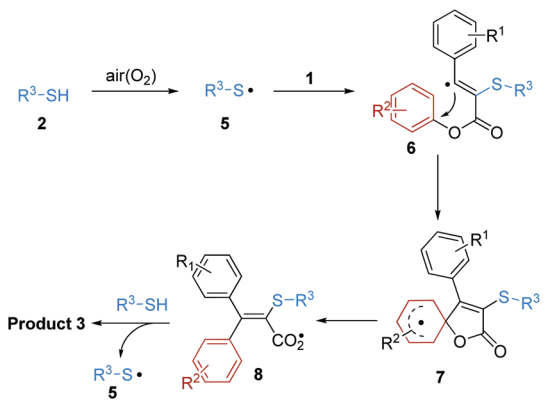
report.[13] Nevertheless, none of the desired products were obtained when alkylalkynoates such as phenyl but-2-ynoate and silyl alkynoates such as phenyl 3-(trimethylsilyl)propiolate were employed under standard conditions.

Subsequently, two control experiments were conducted to explore the possible reaction mechanism. As shown in Scheme 2(a), the model reaction was significantly inhibited when 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added under standard conditions, and TEMPO-trapped complex (*p*-MePhS–TEMPO) was detected by LC-MS analysis (see ESI†). Furthermore, when the reaction of **1a** and PhSSPh was carried out under the standard conditions, no desired product was obtained (Scheme 2(b)). Moreover, the corresponding product **3aa** was obtained in 72% yield and product **3ad** was not detected when the crossover reaction of **1a** with PhSSPh and 4-MePhSH was conducted under standard conditions (Scheme 2(c)). The above results suggested that the present transformation might proceed through a radical process and disulfide was not involved in the present transformation.

Based on the above results and previous reports,[9,10,13,14] a possible reaction pathway of this transformation is proposed as shown in Scheme 3. Initially, the sulfur radical **5** was generated from thiol **2** under air. Then, the selective addition of



Scheme 2 Control experiments.



Scheme 3 Possible reaction pathway.

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sulfur radical **5** to alkynoate **1** gave alkenyl radical **6**. Subsequently, the spiro intermediate **7** was formed through the intramolecular spirocyclization of alkenyl radical **6**. DFT calculations indicated that the spirocyclization of **6** leading to intermediate **7** is kinetically favored over the hydrogen atom transfer from 4-methylbenzenethiol to **6** (see ESI†, Fig. S1), which is consistent with our experimental observations. Next, the migration of the aryl group on the ester moiety *via* cleavage of the C–O bond afforded the carboxyl radical **8**,[10] which reacted with thiol **2** to give the desired product **3** along with the generation of sulfur radical **5** to participate in the next cycle.[13]

Conclusions

In conclusion, a facile and atom-economical method for the synthesis of α-thioacrylic acids has been developed from various aryl alkynoates and thiols. Preliminary mechanistic studies revealed that the reaction might involve a radical process, which proceeded through the cascade thiolation and 1,4-aryl migration of aryl alkynoates. The present reaction could be carried out at room temperature in the absence of any catalyst and additive, offering a simple and efficient route to produce a series of α-thioacrylic acids in moderate to good yields. Further studies of the detailed reaction mechanism and the synthetic applications are currently ongoing in our lab.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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