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α-Benzoyloxylation of β-keto sulfides at ambient temperature†

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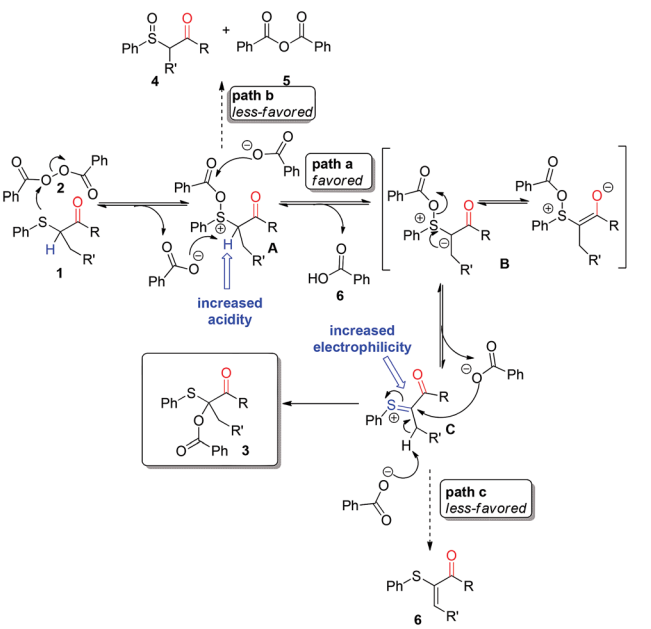
A facile and efficient protocol for the α-benzoyloxylation of β-keto sulfides is presented. This methodology provides a step-economical, mild and practical access to highly functionalized α-*O*-benzoyloxy substituted β-keto sulfides, including those with quaternary carbons, which are not easily obtained through currently available methods.

Introduction

Sulfur-containing compounds are key structural cores of bioactive products, medicinally important compounds, and organic materials and thus, of great chemical relevance.[1] In particular, α-acyloxy sulfides and their analogues are frequently used in various synthetic applications: as valuable precursors in the preparation of complex synthetic intermediates[2] and bioactive natural products.[3] Well-established strategies to prepare these compounds include: (i) Pummerer-type rearrangement of alkyl sulfoxides;[4] (ii) nucleophilic reaction of α-substituted alkyl sulfides;[5] (iii) anti-Markovnikov addition of vinyl esters with arylthiols;[6] (iv) addition of aryl disulfides with (acyloxymethyl)magnesium chlorides;[7] (v) anodic oxidation of sulfides.[8] Recent advances, by Shi *et al.* report that alkyl sulfides can be converted to α-acyloxy sulfides in the presence of hypervalent iodine reagents and tetra-*n*-butylammonium bromide.[9] Alternatively, Yuan developed an elegant gold-catalyzed iodine(III)-mediated direct oxidative acyloxylation of C(sp^3)–H bonds of methyl sulfides.[10] It is interesting to point out that it is known that benzoyl peroxide could undergo decomposition in the presence of organic sulfides[11] to form several products including: sulfoxides, sulfenic acid, olefins, disulfides and α-benzoyloxy substitution adducts. Surprisingly, despite some scattered procedures,[12] typically requiring high reaction temperatures, the relevance of this latter transformation in organic synthesis has been highly overlooked so far. It is likely that this transformation is scarcely described from the point of view of preparation, due to the fact that α-benzoyloxy substituted products are generally obtained in poor chemical yield and/or with low selectivity in combination with significant amounts of the corresponding sulfoxides.

In this work we address a general protocol for the synthesis of α-*O*-benzoyl substituted β-keto sulfides by the reaction strategy shown in Scheme 1. Based on literature, we speculated that the nucleophilic attack of the sulfur atom of a β-keto sulfide **1** on the O–O bond of benzoyl peroxide **2** would form an intermediate sulfonium salt **A** bearing fairly acidic hydrogens, due to the inductive effect of the positive sulfur and the presence of the carbonyl function. We hypothesize that intermediate **A** would be deprotonated at ambient temperature by the benzoate anion (Scheme 1, path a), previously formed during the course of the reaction, leading to a sulfur-stabilized carbonium ion **B** poised



Scheme 1 Uncatalyzed synthesis of α-*O*-benzoyl substituted β-keto sulfides **3**.

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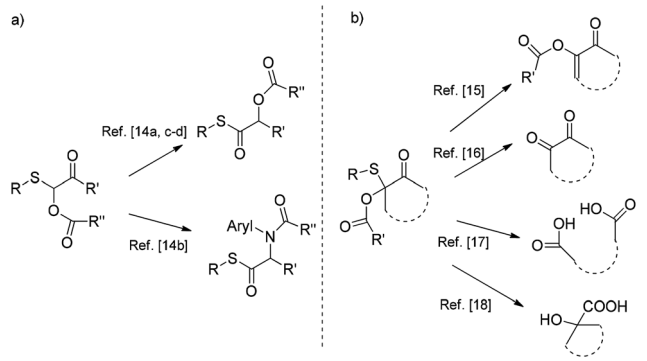


Scheme 2 α-*O*-Acyl-and benzoyl substituted β-keto sulfides in organic synthesis.

to undergo a Pummerer-like rearrangement *via* intermediate **C**. Considering that the alternative path b and c (in the case of disubstituted β-keto sulfides), leading to sulfoxide **4** and α-sulfanyl enone **6** respectively, should be less-favored as a result of both the enhanced α-proton acidity of **A**, as well as the increased electrophilicity of intermediate **C**, provided by the carbonyl group, the preferential formation of **3** with high level of selectivity can be reasonably expected. If successful, the proposed method would provide a general, straightforward, and mild synthetic route to *O*-benzoyloxy β-keto sulfides, avoiding the use of catalysts and saving energy as well as allowing transformation to be carried out at ambient temperature in response to the principle of sustainable chemistry.[13]

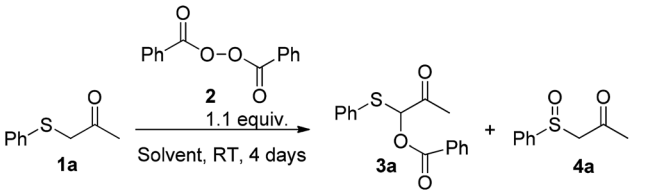
α-Acyloxy β-keto sulfides are important molecules due to their applications in different synthetic fields. Investigations into the reactivity of monosubstituted α-acyloxy β-keto sulfides have established them as valuable intermediates for the synthesis of α-acyloxy-and α-amino-thioester derivatives (Scheme 2; figure a) which can be easily transformed into the corresponding sulfur-free biologically active products.[14] Moreover, disubstituted α-acyloxy β-keto sulfides (Scheme 2; figure b) play a key role as starting materials for the generation of monoenolized diketones,[15] 1,2-diketones,[16] dicarboxylic acids[17] as well as carbocyclic α-hydroxy carboxylic acids.[18] Surprisingly, synthetic strategies for the construction of these latter compounds are scarce and exclusively rely on the use of the Pummerer rearrangement[19] and the acetoxylation reaction of phenyl thio ketones with lead tetraacetate.[20]

Results and discussion

As a proof of concept for our study, the reaction of phenythio acetone **1a** and benzoyl peroxide **2** was carried out in CH_2Cl_2 at room temperature and monitored by GC-MS (Table 1, entry 1).

The investigated reaction took place extraordinarily smoothly without any kind of catalysts to afford **3a** in good conversion (78%) along with only a small amount of the expected by-product sulfoxide **4a** (12%, *via* path b, see: Scheme 1), benzoic acid **6** and benzoic anhydride **5**. These preliminary data indicated that the reaction is spontaneous, efficient and relatively rapid at room temperature. To confirm the reaction

Table 1 Optimization of the reaction conditions[a]

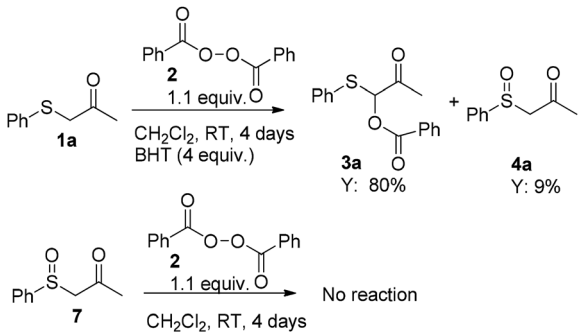


Entry	Solvent	**3a**[b] (%)	**4a**[b] (%)
1	CH_2Cl_2	78	12
2	1,4-Dioxane	79	12
3	Toluene	82	8
4	CH_3COOEt	76	13
5	CH_3CN	71	21
6[c]	EtOH	46	13
7	*n*-Hexane	67	23
8	DMF	74	14
9	THF	75	12
10	DMSO	45	13
11	Acetone	79	11
12[d]	Toluene	87 (78)[e]	9

[a] Reaction conditions: **1a** (333 μmol), benzoyl peroxide **2** (366 μmol), solvent (0.5 mL). [b] GC-MS yield. [c] 23% of 1-ethoxy-1-(phenylthio) propan-2-one was also observed (the formation of this product during the reaction is consistent with our mechanistic proposal). [d] 0.1 mL of solvent was used. [e] Isolated yield.

mechanism, selected control experiments were carried out (Scheme 3). In particular, the reaction was unaffected by the presence of radical scavenger such as butylated hydroxy-toluene (BHT). This result indicate that, as expected, the reaction likely proceeds through a nonradical pathway as illustrated in previously reported studies.[11] Furthermore, sulfoxide **7** failed to afford the corresponding *O*-benzoyloxylation products suggesting the requirement of a nucleophilic sulfur atom other than sufficiently acidic protons in alpha position for the success of this transformation at room temperature.

To further improve the control over the reaction and the conversion, the effect of solvent was investigated. All solvents tested in this study can provide good conversions except EtOH (46%) and DMSO (45%). The best result was obtained with toluene. The expected adduct **3a** can be obtained in 82%



Scheme 3 Control experiments.[a] [a]GC-MS yield.

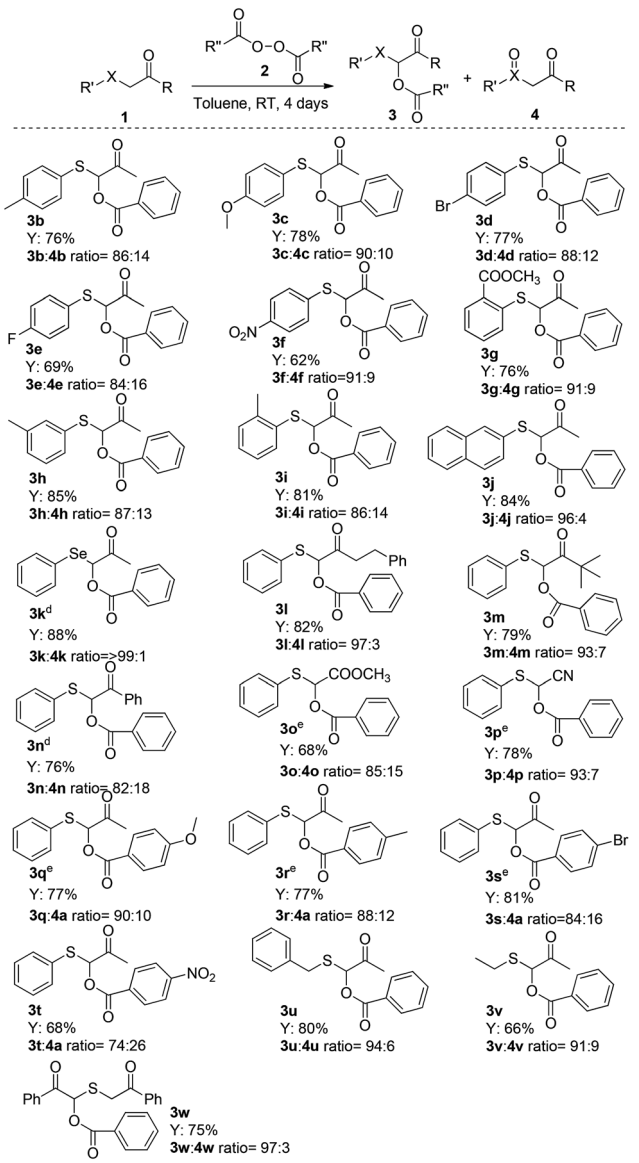
conversion (Table 1, entry 3). Finally, in more concentrated solution the conversion of **3a** could be further increased to 87% (78% isolated yield, entry 12). With the optimal conditions for the α-benzoylation of phenylthioacetone in hand, the scope of the transformation was evaluated with respect to the presence of ring substituents on the phenylthio group (Scheme 4). Various *O*-benzoyl substituted substrates bearing electron-withdrawing (**1f**, **1g**); electron-donating groups (**1b–c**) and alogens (**1d**, **1e**) on the phenyl ring were synthesized using this methodology with high efficiency (69–78% yields; **3 : 4** ratio 84 : 16–91 : 9). Moreover, only a slightly decreased chemical yield (62%; **3 : 4** ratio 91 : 9) was observed in the case of *para*-nitro-substituted β-keto sulfide **1f** despite the relatively lower nucleophilicity of the sulfur atom. Notably, the steric hindrance was very well tolerated in the case of *ortho*-; and *meta*-substituted substrates such as **1i** and **1h** that gave the corresponding *O*-benzoyl substituted compounds **3i** (81%; **3 : 4** ratio 86 : 14) and **3h** (85%; **3 : 4** ratio 87 : 13) in high chemical yield.

Furthermore, naphthylthio ketone **1j** also reacted well, affording the corresponding product **3j** in 84% yield (**3 : 4** ratio 96 : 4). Under the optimized conditions, phenyl selenide ketone **1k** was well tolerated and the product **3k** was obtained in 88% yield and excellent selectivity (**3 : 4** ratio > 99 : 1). Linear (**1l**) and branched (**1m**) 3-alkyl-substituted β-keto sulfides, despite the relatively greater steric hindrance, were both effective in the reaction leading to the desired products in good to high yields (79–82%; **3 : 4** ratio 93 : 7–97 : 3). To our delight, a representative aromatic α-acyloxy β-keto sulfide **1n**, subjected to the same reaction conditions, was smoothly converted into the corresponding product with a good chemical yield (76%; **3 : 4** ratio 82 : 18). On the other hand, 2-(phenylthio)acetonitrile **1p** and methyl 2-(phenylthio)acetate **1o** also reacted with benzoyl peroxide to yield *O*-benzoyl substituted derivatives **3p** (78%; **3 : 4** ratio 93 : 7) and **3o** (68%; **3 : 4** ratio 85 : 15) respectively, albeit much more slowly than the corresponding ketone derivatives, requiring longer reaction times in order to obtain good yields. This seemed to be due to the higher pK_a value of the hydrogens adjacent to the ester and cyano group with respect to the corresponding ketone derivatives which disfavor the formation of the required intermediate **B** (see: Scheme 1). Next, encouraged by the above-mentioned positive results, the applicability of the reaction protocol to other substituted benzoyl peroxides was then preliminary investigated.

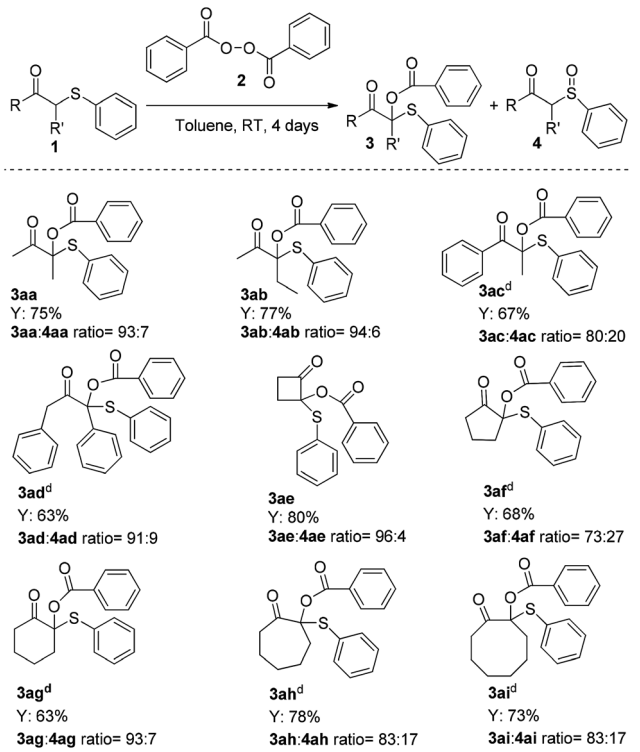
As a result, a decreased yield of **3t** (68%), and the formation of a significant amount of sulfoxide **4** (**3 : 4** ratio 74 : 26) was observed in the case of benzoyl peroxides with a strong electron-withdrawing substituent such as $-NO_2$ on the aromatic ring compared to those with electron-donating group such as **3q** (77% yield; **3 : 4** ratio 90 : 10), **3r** (77%; **3 : 4** ratio 88 : 12) and alogens for example **3s** (81%; **3 : 4** ratio 84 : 16). This behavior may be related to the significantly more electrophilic character of the carbonyl of the benzoyl group (provided by the strong electron-withdrawing group) in intermediate sulfonium **A** which increases the reaction rate of path b (Scheme 1). β-Keto sulfides **1u** and **1v**, bearing an aliphatic group on sulfur performed very well, and delivered regioselectively the corresponding α-benzoyloxy β-keto sulfide **3u** (80%; **3 : 4** ratio 94 : 6) and **3v** (66%; **3 : 4** ratio 91 : 9) in good to high yields. Similarly, **1w** also underwent efficient reaction (75% yield; **3 : 4** ratio 97 : 3) to afford only the mono benzoyloxylation product **3w**.

Finally, the substrate scope was extended to include the synthesis of some challenging α-branched *O*-benzoyloxy β-keto sulfides. As summarized in Scheme 5, gratifyingly acyclic disubstituted β-keto sulfides **1aa–1ad** performed well and delivered the corresponding products **3aa–3ad** in moderate to good yields (63–77%; **3 : 4** ratio 80 : 20–94 : 6).

The reaction proved to be rather general; in addition to acyclic β-keto sulfides, cyclic β-keto sulfides **1ae–1ai** also could be used giving the corresponding quaternary adducts[21] in moderate to high yields (63–80%; **3 : 4** ratio 73 : 27–96 : 4).



Scheme 4 Substrate scope.[a,b,c] [a]Reaction conditions: **1** (333 μmol), benzoyl peroxide (366 μmol), toluene (0.1 mL). [b]Isolated yield. [c]**3** : **4** ratio determined by GC-MS. [d]**3** : **4** ratio determined by ^{1}H NMR. [e]The reaction was carried out for 5 days.



Scheme 5 Substrate scope for the formation of quaternary α-branched *O*-benzoyloxy β-keto sulfides.[a,b,c] [a]Following the general procedure. [b]Isolated yield. [c]**3** : **4** ratio determined by GC-MS. [d]**3** : **4** ratio determined by ^{1}H NMR.

Interestingly, under these very mild reaction conditions, in all the cases examined only trace amount of the corresponding α,β-unsaturated sulfide by-product (Scheme 1, path c), which is the major drawback of the Pummerer reaction,[19d,22] was detected.

Conclusions

In this work a practical and versatile α-benzoyloxylation of β-keto sulfides under mild conditions is demonstrated. Through this procedure, a series of α-benzoyloxy-β-keto sulfides were obtained in moderate to high yields. Besides, α-branched cyclic and acyclic β-keto sulfides were also compatible with the current protocol and provide the corresponding *O*-benzoyloxy β-keto sulfides in moderate to high yields. The wide functional group tolerance highlights the potential of this transformation as an effective method for the operationally simple installation of a benzoyloxy group in the α-position of a sulfur atom in the presence of a carbonyl group. We prospect that the impact of our findings will be beyond the research on sustainable organic synthetic approaches, due to the role of sulfur-bearing compounds in bioactive and medicinally relevant compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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