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T3P® mediated domino C(sp^2)–H sulfenylation/annulation of enaminones and methylsulfinyls for the synthesis of chromone thioether derivatives†

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A new regioselective method for the synthesis of 3-(methylthio)-4*H*-chromen-4-one and 3-(phenylthio)-4*H*-chromen-4-one derivatives has been developed. The reaction between *o*-hydroxy-phenyl-functionalized enaminones and methylsulfinyl derivatives using T3P® gave good yields of chromone thioether derivatives. The reaction proceeds *via* domino chromone ring construction and C(sp^2)–H bond sulfenylation under transition-metal-free conditions.

Introduction

Propylphosphonic anhydride (T3P®) has been commonly used as a water scavenger and a coupling reagent for the synthesis of amides.[1] It has useful properties such as broad functional group tolerance, low toxicity and easy work-up procedures.[2] Because of these reasons, new applications have been recently developed for this reagent.[3] For instance, T3P® has been used in dehydration chemistry that involves the conversion of carboxylic acids and amides into nitriles as in the synthesis of alkenes, isonitriles, and substituted heterocycles.[4] More recently, a convenient microwave assisted T3P® mediated one pot pyrazolone synthesis has been reported.[5] Microwave-assisted organic synthesis (MAOS) is a rapidly growing area in synthetic organic chemistry.[6] Many organic reactions proceed much faster and with higher yields under microwave irradiation when compared to conventional heating.[7] For this reason, this technique has been widely used in organic synthesis.[8] For example, microwave assisted synthesis of 3-sulfenylindoles has been reported using sulfonyl hydrazides.[9]

Chromone or 1,4-benzopyrone is an important scaffold in a large number of natural products with a wide range of biological activities.[10] The vast range of biological effects associated with this scaffold has resulted in the chromone ring system being considered as a privileged structure.[11] 3-Sulfenylated chromones, a class of the chromone family having alkyl or aryl thioether linkage at the 3-position of the chromone moiety, have found extensive application in synthetic chemistry.[12] Recently, 3-sulfenylated chromone derivatives were tested for their antitumor activity against human solid tumor cell lines including HCCLM-7, Hep-2, MDA-MB-435S and SW-480.[13]

The reactions involving C–S bond formation are important routes to install sulphur fragments into organic compounds.[14] The C(sp^2)–S bonds such as C–S (sulfenyl) bonds play a key role in controlling the physical properties and biological activities of sulphur containing compounds.[15] Development of novel and efficient methodologies to generate C(sp^2)–S bonds has attracted great attention of many organic chemists.[16] Several methods are available for generating thioether molecules with different sulfenylating reagents such as thiols, sulfonylchlorides, silver(I) trifluoromethanethiolate, disulfides, sodium sulfinates, sulphur powder and sulfonylhydrazides.[17–19] In this connection, widespread methodologies are available in the literature for the construction of C(sp^2)–S bonds *viz.* the transition-metal-catalysed Ullman reaction,[20] the Chan–Lam cross-coupling reaction along with the transition-metal-catalysed C–H bond activation.[21,22] In recent times, as a new development, the transition-metal-free oxidative coupling has emerged as a powerful complementary approach in C–S bond forming reactions.[23] The transition metal-free cross coupling reaction has several advantages. These metal-free[24] cross coupling reactions are often practical, as they are generally less sensitive to air and moisture. Furthermore, transition metals are associated with drawbacks such as cost, toxicity, need for non-commercial ligands and threshold values in pharmaceutical products. The metal free cross-coupling transformations have been successfully employed in the synthesis of many useful organic compounds elaborated with sulfenyl groups.

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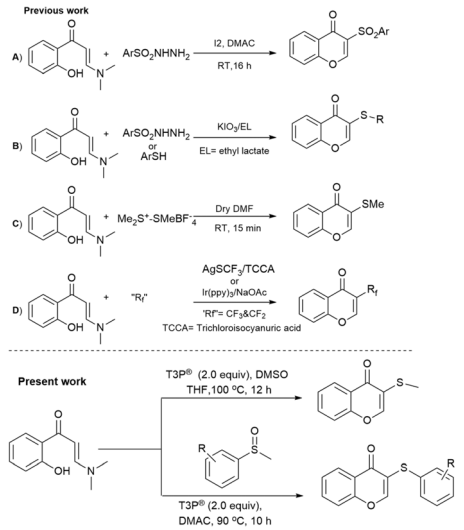


Fig. 1 Synthetic approach of 3-sulfenylated chromone.

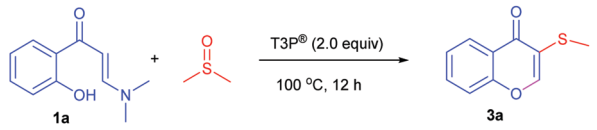
Wan and co-workers have reported iodine mediated radical C(sp^2)–H sulfonylation and C(sp^2)–N bond oxygenation enabling the chemoselective synthesis of 3-sulfonylated chromones by using enaminones and sulfonylhydrazines[12d] (Fig. 1A). On the other hand, the same group introduces the similar methodologies for making 3-sulfenylated chromones from enaminone using sulfonylhydrazines and thiophenols *via* a KIO_3-catalyzed domino reaction[12h,k] (Fig. 1B). The only difference in the methodology is the use of KIO_3 instead of iodine for radical C(sp^2)–H sulfenylation. However, the Yokoe group in 1994 first reported the preparation of 3-methylthiochromone by the reaction of dimethyl(methylthio)sulfoniumtetrafluoroborate with enaminone[12j] (Fig. 1C). Later on in 2014, a facile and efficient synthetic strategy has been reported by the Yang group using $AgSCF_3$ and trichloroisocyanuric acid[12a] (Fig. 1D).

Most of the methods reported to date for the preparation of 3-sulfenylated chromones used NH_4I, KIO_3 and I_2 as oxidants. However to the best of our knowledge, T3P® has not been used for the preparation of 3-sulfenylated chromones using enaminones. In our continuous effort to prepare natural product hybrids,[25] we developed interest in preparing the chromone thioether derivatives. Earlier, we have reported the preparation of chromone using T3P®.[26] Herein, we report our work on this interesting new methodology for the preparation of 3-sulfenylated using T3P®.

Results and discussion

During the course of our development of a synthetic methodology for the preparation of chromones using enaminone, it was found that when enamino ketone **1** was reacted with T3P® in the presence of DMSO, 3-suflenylated chromone was formed. Surprised by this result, we planned to investigate the sulfenylation reaction further to develop a new synthetic methodology. At the beginning, the reaction of enaminone with DMSO was tentatively run in the presence of T3P at room temperature and the 3-sulfenylated product **3a** was obtained in 10% yield (Table 1, entry 1). Inspired by this preliminary result, we screened the cyclization reaction in

Table 1 Screening optimization conditions[a]



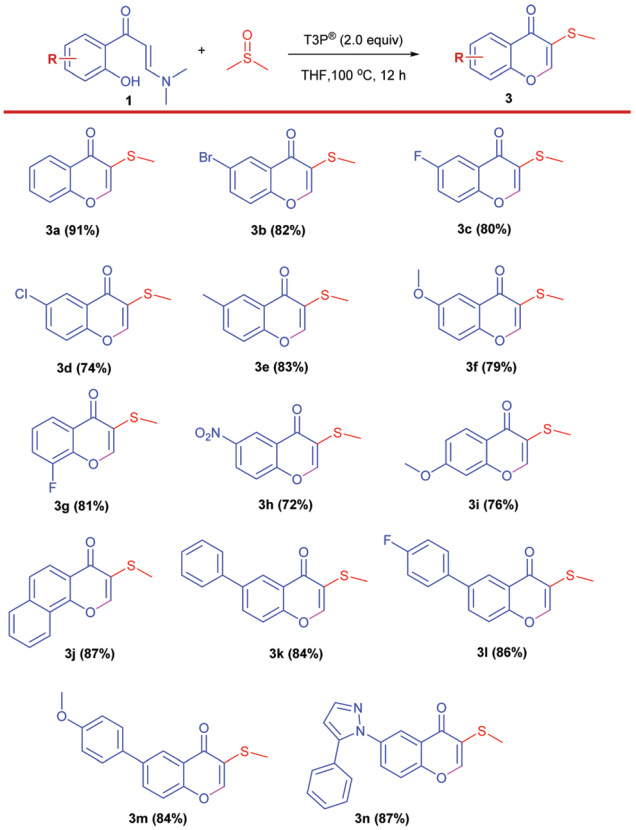
Entry	T3P® [equiv.]	Solvent	T [°C]	DMSO [equiv.]	Yield[b] [%]
1	1.0	EtOAc	RT	3.0	10
2	1.0	EtOAc	60	3.0	25
3	2.0	EtOAc	60	3.0	40
4	2.0	EtOAc	60	1.0	5
5	2.0	EtOAc	100	2.0	20
6	2.0	EtOAc	100	5.0	59
7	2.0	DMAC	100	5.0	56
8	2.0	DMF	100	5.0	52
9	2.0	THF	100	5.0	63
10	2.0	THF	100	8.0	91
11	2.0	EtOAc	100	8.0	83
12	2.0	DMAC	100	8.0	73
13	2.0	EtOAc	130	8.0	47
14	2.0	EtOAc	100	20.0	61
15	3.0	EtOAc	100	8.0	57
16	2.0	Me_2SO_4	100	—	60[c]
17	—	EtOAc	100	8.0	0

[a] General conditions: enaminone **1a** (1.0 equiv.), DMSO (8.0 equiv.), T3P® (2.0 equiv.), THF (1 mL), 100 °C. All reactions were run for 10 h. [b] Yields of isolated products from enaminone. DMAC = *N*,*N*-dimethylacetamide. [c] Chromone [**1b**].

different reaction media and THF (Table 1, entry 10) was the most favourable reaction medium. Further investigation revealed that increasing the temperature to 60 °C gave the product in only 25% yield (Table 1, entry 2). Further increasing the temperature to 100 °C does increase the yield of the reaction. When the amount of DMSO was varied, it was found that 8.0 equivalents of DMSO are optimal. But the use of excess DMSO and T3P® for the sulfenylation reaction under the same reaction conditions did not increase the yield much (Table 1, entries 14 and 15) which indicated that it was sufficient to have 8.0 equivalents of DMSO. We have also attempted the cyclisation reaction at elevated temperatures however we did not have better result (Table 1, entry 13). Finally, to validate that the sulfenylation reaction was mediated by T3P®, a control experiment was conducted. As expected, treating compound **1a** and DMSO (8.0 equiv.) in EtOAc at 100 °C without T3P® for 12 h gave only zero conversion (Table 1, entry 17). Also, when the reaction was performed taking dimethyl sulphate instead of DMSO we did not observe any product formation (Table 1, entry 16) which showed that DMSO acts as a thiomethyl source in the reaction.

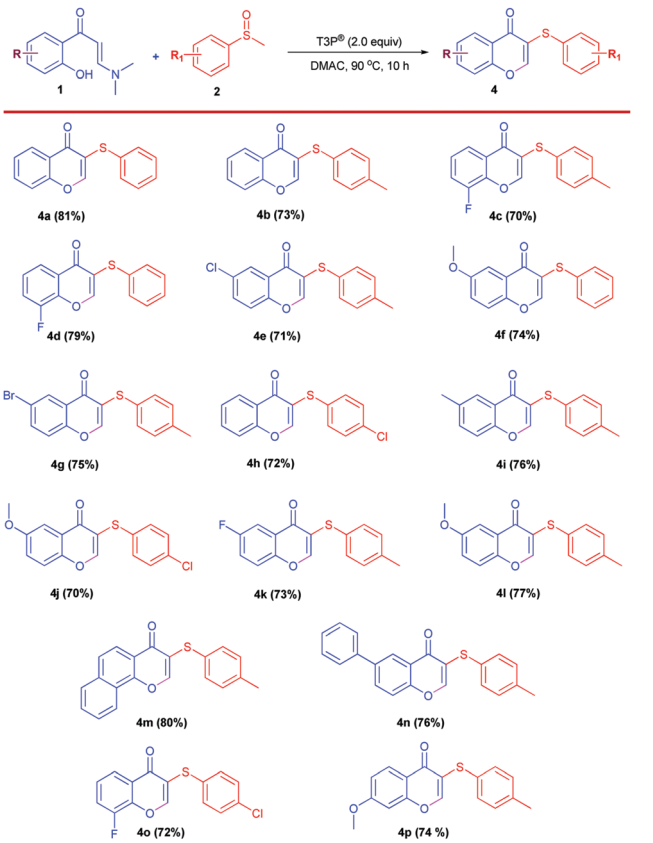
To prove the generality of this method, various substituted aryl enaminones were examined and the results are summarized in Table 2. More importantly previously inaccessible naphthalene analogues and pyrazole analogues were synthesized in very good yield (compounds **3j** and **3n**). Also, there is no effect on the yield of the sulfenylation reaction upon aromatic ring substitution (*ortho* as well as *para* substituted enaminones gave similar yields). It can be found that substrates having electron-donating groups (CH_3 and OMe) gave little higher yields than electron-deficient groups (NO_2 and Cl). The advantages of using T3P® in the sulfenylation reaction compared to other available

Table 2 Scope of 3-sulfenylated chromones using T3P® and DMSO[a,b]



[a] General conditions: enaminone **1a** (1.0 equiv.), DMSO (8.0 equiv.), T3P® (2.0 equiv.), THF (1 mL) 100 °C. All reactions were run for 12 h. [b] Yields of isolated products from enaminone **1**. T3P® (50% in EtOAc solution).

Table 3 Scope of 3-sulfenylated chromones using T3P® and aryl methylsulfoxide[a,b]



[a] General conditions: enaminone **1a** (1.0 equiv.), aryl methyl sulfoxide (2.0 equiv.), T3P® (2.0 equiv.), DMAC (0.3 mL), 90 °C. All reactions were run for 10 h. [b] Yields of isolated products from enaminone **1**. DMAC = *N*,*N*-dimethylacetamide. T3P® (50% in EtOAc solution).

methods are low toxicity, non-allergenic, water soluble by products and mild reaction conditions. This is the reason for T3P® being classified as a green reagent. Based on the above results, we want to explore other commercially available sulfoxide for the sulfenylation reaction with enaminone **1**. When di-phenyl sulfoxide was used, we did not observe any sulfenylation reaction instead only chromone was isolated. But taking methyl phenylsulfoxide we could get 3-thioaryl-chromone in good yield. After screening the optimal conditions, various substituted enaminones were subjected to the sulfenylation reaction using methyl phenylsulfoxide and the results are summarised in Table 3. All the 3-thioaryl-chromones were well characterized by ^{1}H-NMR, ^{13}C-NMR and LC-MS data. The yields obtained in the sulfenylation reaction with methyl phenylsulfoxide were moderate to good.

To investigate the possible process of the reaction, few control experiments were designed and conducted as outlined in Fig. 2. Thus, when the chromone **1b** was treated with T3P® in the presence of DMSO at 100 °C for 12 h, no product was formed. The result indicate that annulation to chromone is not the initial step in the reaction. The next step was the sulfenylation reaction of enaminone with T3P® and di-phenylsulfoxide. Chromone **1b** was formed instead of **3a** when di-phenylsulfoxide was considered as the sulfenylation source. We conclude that the

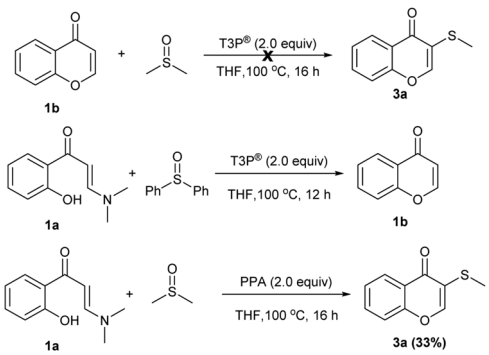


Fig. 2 Control experiments.

presence of one methyl group in the sulfoxide reagent is must for the success of the sulfenylation reaction. Furthermore, we performed a reaction in PPA instead of T3P® under the same conditions to obtain the product in only 33% yield.

A plausible reaction mechanism of the deaminative sulfenylation was proposed in Fig. 3. The first step of this mechanism is the nucleophilic attack of oxygen atoms of DMSO to form T3P®-complex **III**. The 2nd nucleophilic attack of enaminone on T3P® methyl

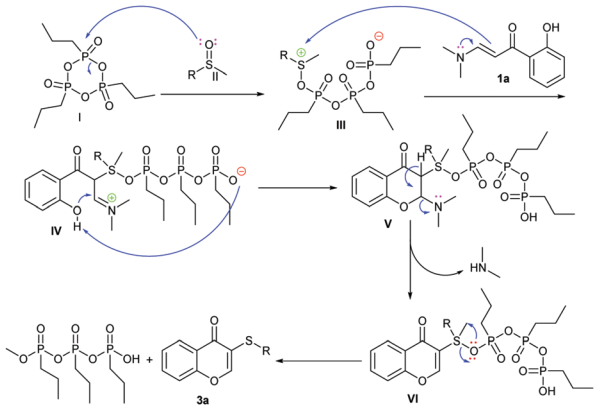


Fig. 3 Plausible mechanism of 3-sulfenylated chromone.

sulfoxide complex **III** to neutralize sulfonium ions generated complex **IV** which undergoes cyclization to form cyclic intermediate **V**. Intermediate **V** undergoes the E1cb mechanism to eliminate dimethyl amine and form 3-sulfinyl-chromone derivative **VI**. The sulfinyl complex **VI** undergoes intramolecular methyl transfer to form the final compound **3a**. This explains the basic requirement of one methyl group in the sulfinyl complex **VI** for the success of the T3P® catalyzed sulfenylation reaction using methyl sulfinyls.

Conclusions

In summary, a new methodology has been established by the reaction between *o*-hydroxyphenyl-functionalized enaminones and methylsulfinyl derivatives using T3P® *via* domino chromone ring construction and C(sp^2)–H bond sulfenylation under transition-metal-free conditions. This is the first report of T3P® mediated preparation of 3-sulfenylated chromone. We believe that this method will find wide spread application in the synthesis of sulfenylated chromone derivatives.

Experimental section

General procedure for the synthesis of 3-(methylthio)-4*H*-chromen-4-one (3a)

Enaminone **1a** (100 mg, 0.523 mmol) was added to a dried sealed tube containing DMSO (0.297 mL, 4.18 mmol) in THF (1 mL) followed by the addition of 50% T3P® in EtOAc (343 mg, 1.04 mmol) at 10 °C. After 15 min, the reaction mixture was heated to 100 °C for 12 h. The reaction progress was monitored by TLC. Then the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with water and brine, dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, hexane/EtOAc) to give desired product **3a** (91%) as a colourless solid. The same procedure was used to prepare compounds **3b–3n**.

General procedure for the synthesis of 3-(phenylthio)-4*H*-chromen-4-one (4a)

Enaminone **1a** (100 mg, 0.523 mmol) was added to a dried sealed tube containing DMAC (0.3 mL) followed by the addition of 50% T3P® in EtOAc (343 mg, 1.04 mmol) and methyl phenyl sulfoxide (145 mg, 1.04 mmol) at 0 °C. After 15 min, the reaction mixture was heated to 90 °C for 10 h. The reaction progress was monitored by TLC. Then the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with water and brine, dried with anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified by flash chromatography (silica gel, hexane/EtOAc) to give desired product **4a** (81%) as a colourless solid. The same procedure was used to prepare compounds **4b–4p**.

Conflicts of interest

There are no conflicts of interest.

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