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RESEARCH ARTICLE

A facile and rapid one-pot synthesis of 1,4-diaryl-2-mercaptoimidazoles under solvent-free conditions

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A highly efficient and green synthesis of 1,4-diaryl-2-mercaptoimidazoles **4** is described. Potassium carbonate catalysed reaction of α-tosyloxyacetophenones **1** with various anilines **2** afforded α-anilinoacetophenones **3**, which *in situ* underwent cyclization with potassium thiocyanate and *p*-toluenesulphonic acid in solvent-free conditions to yield 1,4-diaryl-2-mercaptoimidazoles **4** in excellent yield. This one-pot protocol offers a useful modification as it has advantages of short reaction times, cleaner reaction profiles and simple work-up that exclude use of toxic solvents.

Keywords: α-Tosyloxyacetophenones; α-Anilinoacetophenones; 1,4-Diaryl-2-mercaptoimidazoles; Solvent-free

1. Introduction

Imidazoles constitute an important class of heterocyclic compounds and specifically, 2-mercaptoimidazoles have been found to be an integral part of pharmacologically active compounds that display significant antimicrobial [1], H^+/K^+-ATPase inhibitor [2], H_3-receptor antagonist [3], and neuropeptide Y5-receptor antagonist [4, 5] activities. 2-Mercaptoimidazoles are also of general synthetic utility since they permit functional group and structural modifications to synthesize imidazole [6], imidazo[2,1-*b*]thiazole [7], imidazo[1,2-*d*][1,2,4]thiadiazole [8] etc.

A perusal of literature revealed that most common synthesis of 2-mercaptoimidazoles involved the condensation of α-aminoacetophenones with potassium thiocyanate in acetic acid (Marckwald Synthesis). Generally, the synthesis of α-aminoacetophenones are accomplished by oxidation of β-hydroxyamines [9, 10], reaction of α-haloketones with anilines in the presence of variety of bases [11–14], reaction of anilines with diazoacetophenones in the presence of metal catalyst [15–17], oxidative cleavage of C−C double bond of allylamines [18], reaction of α-iodoxybenzoic acid with aziridines [19] and reaction of amines with

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ketonyl-Pt(II) dinuclear complexes [20]. α-Aminoketones have also been prepared recently by the N-H insertion of rhodium carbene intermediates derived from α-diazocarbonyl compounds with anilines [21]. However, some of these methods demand for highly lachrymatory, toxic, sophistically designed reagents or substrates, multistep synthesis, extreme temperature conditions and α-aminoketones are somewhat unstable in some cases. Consequently, there is a need for an alternative approach, which does not involve the isolation of α-aminoketones and provides safer and milder conditions.

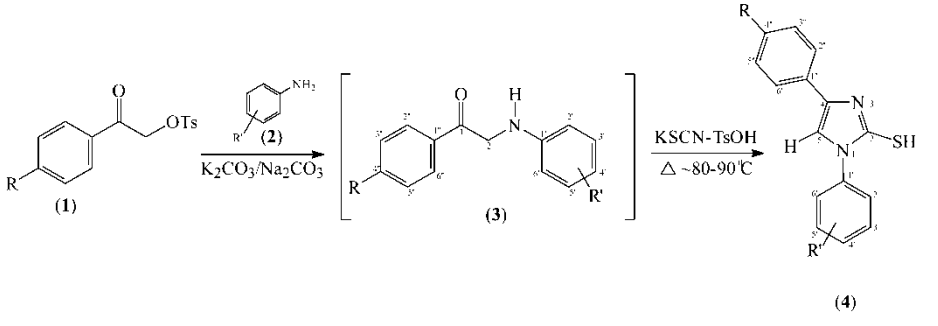
2. Results and discussion

Recently, organic synthesis under solvent-free conditions have gained much attention due to advantages over the conventional methods in terms of enhanced selectivity, cleaner reaction profiles, ease of manipulation and relatively benign conditions. In view of these observations and in continuation of our ongoing interest to develop greener protocols [22–24], we herein report solvent-free synthesis of α-anilinoacetophenones **3** and their *in situ* conversion into 1,4-diaryl-2-mercaptoimidazoles **4** starting from α-tosyloxyacetophenones **1**.

The general method to prepare the title compounds is outlined in scheme 1. The synthesis of 2-mercaptoimidazoles was first attempted in a stepwise manner *via* the isolation of intermediate, α-anilinoacetophenones **3**. The reported α-tosyloxyacetophenones **1** were ground with appropriately substituted anilines **2** in solvent-free conditions to give **3** in 45–62% yield. To optimize the yields further, we explored the reaction by adding catalytic amount of base sodium/potassium carbonate to the above reaction mixture. Intimate grinding of the contents gave the exclusive and rapid formation of **3** in excellent yield (81–96%) within 3–5 min (See table 1). It is worth mentioning here that when Prakash *et al*. carried out the base catalysed reaction of α-tosyloxyacetophenones and anilines in ethanol, an additional product, 1,4-diaryl-2-(arylamino) but-2-ene-1,4-dione **5**, was produced [25]. (See scheme 2)

Furthermore, condensation of **3** with potassium thiocyanate was carried out by thoroughly mixing and heating the contents to about 80–90 °C for 5–10 min in the presence of *p*-toluenesulphonic acid. The reaction afforded the expected 1,4-diaryl-2-mercaptoimidazoles **4** in 65–82% yields (see table 1). The most probable mechanism for this reaction seems to be analogous to that of Marckwald Synthesis [26].

Encouraged by the success of stepwise procedure, a one-pot synthesis of **4** was also developed where **1** was converted to **4,** *in situ*. The one-pot procedure afforded better yields of **4** than the step-wise manner. A one-pot synthesis of 2-mercaptoimidazole is also mentioned in the literature, but that includes the use of solvents like acetonitrile and acetic acid, and the yields were not as high as in the present synthesis [27]. The generality of the reaction was

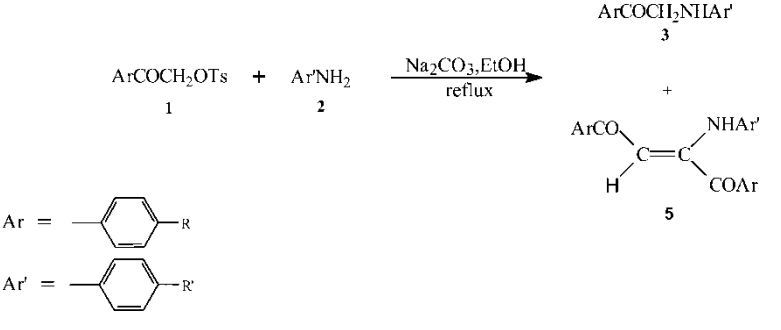


SCHEME 1

Table 1. Physical data of the synthesized compounds **3**[a] and **4**[b].

Compound	**R**	**R′**	Mp[c] (°C) (ref.)	Yields (%)
3a	H	H	99[28]	95 (60)
3b	H	*p*-F	130	92 (62)
3c	F	H	128[29]	95 (55)
3d	F	*p*-Cl	180[30]	96 (59)
3e	F	*p*-OCH_3	175	91 (52)
3f	F	*p*-F	132[29]	90 (56)
3g	Cl	*o*-OCH_3	135	81 (45)
3h	OCH_3	*m*-NO_2	142	88 (50)
4a	H	H	214[31]	85 (66)
4b	H	*p*-F	206	75 (67)
4c	F	H	232	80 (69)
4d	F	*p*-Cl	248	65 (52)
4e	F	*p*-OCH_3	260 (deco.)	72 (71)
4f	F	*p*-F	246	70 (65)
4g	Cl	*o*-OCH_3	232	82 (72)
4h	OCH_3	*m*-NO_2	244 (deco.)	79 (68)

Note: a. Yields in the parenthesis are for the experiment without Na_2CO_3/K_2CO_3.
b. Yields in the parenthesis are for stepwise procedure (not for one-pot experiment).
c. Melting points were determined in open capillaries in electrical apparatus and are uncorrected.



SCHEME 2

established by using differently substituted anilines and α-tosyloxyacetophenones and also by upgrading the reaction successfully from milligram to gram scale.

The known products were identified by comparison of m.p.'s with those reported in the literature [28–31]. The structures of novel compounds were confirmed on the basis of their spectral (IR, ^{1}H, ^{13}C NMR) and combustion analysis data. Finally, the present study provides a facile, rapid and high yielding protocol for synthesis of α-anilinoacetophenones **3** and 1,4-diaryl-2-mercaptoimidazoles **4** from readily available α-tosyloxyacetophenones under solvent-free conditions.

3. Experimental

The IR spectra of the compounds were recorded on Buck Scientific IR M-500 spectrophotometer using KBr pellets (ν_{max} in cm^{-1}), ^{1}H and ^{13}C NMR spectra on a Bruker instrument at 300 and 75 MHz, respectively; chemical shifts are expressed in δ-scale downfield from TMS as an internal standard.

3.1 *General procedure for the synthesis of α-anilinoacetophenones 3 from α-tosyloxyacetophenones 1*

A mixture of **1** (1 mmol), appropriate aniline **2** (1.2 mmol) and a pinch of anhydrous Na_2CO_3 or K_2CO_3 was placed in a dry pestle and mortar and ground thoroughly. After 2–3 min, an exothermic reaction took place and temperature increased to about 45 °C. A yellow colored solid so obtained was washed well with ice-cold water to remove the Na_2CO_3 or K_2CO_3, dried and crystallized from ethanol.

3.1.1 Synthesis of α-(*o*-methoxyanilino)-*p*-chloroacetophenones 3 g on large scale. A mixture of α-tosyloxy-p-chloroacetophenone **1** (10 mmol, 3.2 g), *o*-anisidine **2** (12 mmol, 1.48 g) and a pinch of anhydrous Na_2CO_3 was placed in a dry pestle and mortar and ground thoroughly. After 2–3 min, an exothermic reaction took place and the temperature rose to about 50 °C. A yellow colored solid so obtained was washed well with ice-cold water to remove the Na_2CO_3, dried and crystallized from ethanol to give pale crystal (2.5 g, 69%).

Compound 3b. (Found N, 6.01 $C_{14}H_{12}FNO$ required N, 6.11) IR ($\nu_{max,}$ cm^{-1}): 3345 (N-H), 1680.1(CO); ^{1}H NMR (300 Hz; $CDCl_3$)δ_H 4.61 (2H, s, CH_2), 6.63–6.70 (2H, m, 2′, 6′-H), 6.91–6.99 (2H, m, 3′, 5′-H), 7.52–7.57 (2H, m, 3″, 5″-H), 7.63–7.68 (1H, m, 4″-H), 8.02–8.05 (2H, m, 2″, 6″-H); ^{13}C NMR (75 Hz; $CDCl_3$)δ_C 50.91 (C-2), 113.81 (d, J = 7.5 Hz, C-2′, 6′), 115.81 (d, J = 21.7 Hz, C-3′, 5′), 127.75 (C-3″, 5″), 128.91 (C-2″, 6″), 133.91 (C-4″), 134.89 (C-1″), 143.55 (C-1′), 156.05 (d, J = 234.0 Hz, C-4′), 195.1 (C-1).

Compound 3e. (Found N, 5.33 $C_{15}H_{14}FNO_2$ required N, 5.40) IR ($\nu_{max,}$ cm^{-1}): 3399.7 (N-H), 1682.2 (CO); ^{1}H NMR (300 Hz; $CDCl_3$)δ_H 3.78 (3H, s, OCH_3), 4.57 (2H, s, CH_2), 6.69 (2H, d, J = 8.4 Hz, 3′, 5′-H), 6.84 (2H, d, J = 8.4 Hz, 2′, 6′-H), 7.16–7.24 (2H, m, 3″, 5″-H), 8.04–8.09 (2H, m, 2″, 6″-H); ^{13}C NMR (75 Hz; $CDCl_3$)δ_C 49.3 (C-2), 55.51 (OCH_3), 114.05 (C-3′, 5′), 115.31 (C-2′, 6′), 116.15 (d, J = 21.7 Hz, C-3″, 5″), 130.55 (d, J = 5.25 Hz, C-2″, 6″), 131.22 (d, J = 3 Hz, C-1″), 140.20 (C-1′), 143.55 (C-1′), 155.23 (C-4′), 166.21 (d, J = 254.25 Hz, C-4″), 192.13 (C-1).

Compound 3g. (Found N, 5.05 $C_{15}H_{14}ClNO_2$ required N, 5.08) IR ($\nu_{max,}$ cm^{-1}): 3412.7 (N-H), 1685.5 (CO); ^{1}H NMR (300 Hz; $CDCl_3$)δ_H 3.92 (3H, s, OCH_3), 4.61 (2H, s, CH_2), 6.60–6.94 (4H, m, 2′, 3′, 5′, 6′-H), 7.51 (2H, d, J = 8.7 Hz, 3″, 5″-H), 7.99 (2H, d, J = 8.7 Hz, 2″, 6″-H); ^{13}C NMR (75 Hz; $CDCl_3$)δ_C 50.31 (C-2), 55.49 (OCH_3), 109.72 (C-3′), 110.13 (C-4′), 117.30(C-5′), 121.16(C-6′), 129.17 (C-3″, 5″), 129.21 (C-2″, 6″), 133.43 (C-1′), 137.07 (C-4″), 140.18 (C-1″), 143.55 (C-1′), 147.23 (C-2′), 194.00 (C-1).

Compound 3h. (Found N, 9.68 $C_{15}H_{14}N_2O_4$ required N, 9.79) IR ($\nu_{max,}$ cm^{-1}): 3399.1 (N-H), 1680.2 (CO); ^{1}H NMR (300 Hz; $CDCl_3$)δ_H 3.93 (3H, s, OCH_3), 4.62 (2H, s, CH_2), 7.01–7.04 (3 H, m, 6′, 3″, 5″-H), 7.31–7.36 (1H, m, 5′, -H), 7.47 (1H, s, 2′-H), 7.59 (1H, d, J = 7.5 Hz, 4′-H); 8.04 (2H, d, J = 7.8 Hz, 2″, 6″-H); ^{13}C NMR (75 Hz; $CDCl_3$)δ_C 49.36 (C-2), 55.58 (OCH_3), 106.05 (C-2′), 112.37 (C-4′), 114.20 (C-3″, 5″), 119.59 (C-6′), 127.48 (C-1″), 129.78 (C-5′), 130.17 (C-2″, 6″), 147.83 (C-3′), 149.52 (C-1′), 164.38 (C-4″), 192.31 (C-1).

3.2 *General procedure for the synthesis of 1,4-diaryl-2-mercaptoimidazoles 4 from α-anilinoacetophenones 3 (Modified Marckwald Synthesis)*

3 (1 mmol), potassium thiocyanate (5 mmol) and *p*-toluenesulphonic acid (5 mmol) were ground vigorously using a pestle and mortar. The contents were transferred to a conical flask and heated to 80–90 °C for 5–10 min. A yellow colored solid was obtained which was washed with water, filtered, dried and crystallized from ethanol.

3.3 *General procedure for the one-pot synthesis 1,4-diaryl-2-mercaptoimidazoles 4 from 1*

α-Tosyloxyacetophenone **1** (1 mmol), aniline **2** (1.2 mmol) and a pinch of anhydrous Na_2CO_3 or K_2CO_3 were ground thoroughly in a pestle and mortar for 2–3 min. When a yellow colored solid was obtained, potassium thiocyanate (5 mmol) and *p*-toluenesulphonic acid (5 mmol) was added to it and further grinding was done for another 5 min. The contents were heated to 80–90 °C in a conical flask for 5–10 min. A yellow color solid was obtained which was filtered after the addition of water, washed with water to remove excess of *p*-toluenesulphonic acid, dried and crystallized from ethanol.

Compound 4b. (Found N, 10.11 $C_{15}H_{11}FN_2S$ required N, 10.37) IR ($\nu_{max,}$ cm^{-1}): 3045 (S-H); ^{1}H NMR (300 Hz; $CDCl_3$)δ_H 7.08 (1H, s, 5-H), 7.18–7.24 (2H, m, 3′, 5′-H), 7.32–7.43 (3H, m, 3″, 4″, 5″-H), 7.56–7.59 (2H, m, 2″, 6″-H), 7.61–7.66 (2H, m, 2′, 6′-H), 12.5 (1 H, bs, S-H, exchangeable with D_2O); ^{13}C NMR (75 Hz; $CDCl_3$)δ_C 114.96 (C-5), 116.19(d, J = 22.5 Hz, C-3′, 5′), 124.9 (C-3″, 5″), 127.16 (C-4), 128.05 (d, J = 8.3 Hz, C-2′, 6′), 128.62 (C-4″), 129.21 (C-2″, 6″), 130.28 (C-1″), 133.55 (C-1′), 161.7 (C-2).

Compound 4c. (Found N, 10.03 $C_{15}H_{11}FN_2S$ required N, 10.37) IR ($\nu_{max,}$ cm^{-1}): 3057 (S-H); ^{1}H NMR (300 Hz; $CDCl_3$+DMSO-d_6)δ_H 7.07–7.13 (3 H, m, 5, 3″, 5″-H), 7.47–7.67 (7H, m, 2′, 3′, 4′, 5′, 6′, 2″, 6″-H), 12.7 (1 H, bs, S-H, exchangeable with D_2O);^{13}C NMR (75 Hz; $CDCl_3$+DMSO-d_6)δ_C 113.42 (C-5), 115.08(d, J = 22.5 Hz, C-3″, 5″), 123.6 (d, J = 3.75 Hz, C-1″), 124.96 (C-2′, 6′), 125.52 (d, J = 8.3 Hz, C-2″, 6″), 127.30 (C-4′), 127.86 (C-4), 128.05 (C-3′, 5′), 136.81 (C-1′), 161.4 (d, J = 246 Hz, C-4″), 161.81 (C-2).

Compound 4d. (Found N, 9.28 $C_{15}H_{11}FN_2S$ required N, 9.195) IR ($\nu_{max,}$ cm^{-1}): 3044 (S-H);^{1}H NMR (300 Hz; $CDCl_3$+DMSO-d_6)δ_H 7.10–7.13 (3H, m, 5, 3″, 5″-H), 7.49 (2H, d, J = 9 Hz, 3′, 5′-H), 7.62 (4H, m, 2′, 6′, 2″, 6″-H), 12.76 (1H, bs, S-H, exchangeable with D_2O);^{13}C NMR (75 Hz; $CDCl_3$+DMSO-d_6)δ_C 114.03 (C-5), 116.10 (d, J = 22.5 Hz, C-3″, 5″), 123.9 (C-1″), 126.55 (d, J = 8.3 Hz, C-2″, 6″), 127.24 (C-2′, 6′), 128.5 (C-4), 129.19 (C-3′, 5′), 133.99 (C-4′), 136.21 (C-1′), 162.4 (C-2), 162.54 (d, J = 247 Hz, C-4″).

Compound 4e. (Found N, 9.27 $C_{15}H_{11}FN_2S$ required N, 9.33) IR ($\nu_{max,}$ cm^{-1}): 3036 (S-H); ^{1}H NMR (300 Hz; $CDCl_3$)δ_H 3.87 (3H, s, OCH_3), 6.993 (1H, s, 5-H), 7.02 (2 H, d, J 9 Hz, 3′, 5′-H), 7.06–7.12 (2H, m, 3″, 5″-H), 7.49–7.56 (4H, m, 2′, 6′, 2″, 6″-H);^{13}C NMR (75 Hz; $CDCl_3$)δ_C 55.55 (OCH_3), 114.43 (C-3′, 5′), 115.0 (C-5), 116.32(d, J = 21.7 Hz, C-3″, 5″), 123.69 (C-1″), 126.7(d, J = 8.3 Hz, C-2″, 6″), 127.32 (C-2′, 6′), 128.89 (C-4), 130.32 (C-1′), 159.59 (C-4′), 162.5 (C-2), 162.64 (d, J = 246 Hz, C-4″).

Compound 4f. (Found N, 9.68 $C_{15}H_{11}FN_2S$ required N, 9.72) IR ($\nu_{max,}$ cm^{-1}): 3037 (S-H); ^{1}H NMR (300 Hz; $CDCl_3$+DMSO-d_6)δ_H 7.03 (1H, s, 5-H), 7.07–7.23 (4H, m, 2′, 6′, 2″, 6″-H), 7.58–7.64 (4H, m, 3′, 5′, 3″, 5″-H), 12.64 (1 H, bs, S-H, exchangeable with D_2O); ^{13}C NMR (75 Hz; $CDCl_3$+DMSO-d_6)δ_C 113.97 (C-5), 115.64(d, $J = 23.2$ Hz, C-3″, 5″), 115.75 (d, $J = 21.7$ Hz, C-3′, 5′), 123.73 (C-1″), 126.21 (d, $J = 8.3$ Hz, C-2″, 6″), 127.64 (d, $J = 8.3$ Hz, C-2′, 6′), 128.60 (C-4), 133.58 (C-1′), 161.64 (d, $J = 246$ Hz, C-4″), 162.14 (d, $J = 246$ Hz, C-4′), 162.91 (C-2).

Compound 4g. (Found N, 8.53 $C_{16}H_{13}ClN_2OS$ required N, 8.84) IR ($\nu_{max,}$ cm^{-1}): 3049 (S-H);^{1}H NMR (300 Hz; $CDCl_3$)δ_H 3.85 (3H, s, OCH_3), 7.05–7.51 (9H, m, 5, 3′, 4′, 5′, 6′, 2″, 3″, 5″, 6″-H);^{13}C NMR (75 Hz; $CDCl_3$)δ_C 60.64 (OCH_3), 117.16 (C-5), 121.51 (C-6′), 123.52 (C-4), 125.29 (C-5′), 130.54(C-3″, 5″), 130.85(C-1′), 131.65 (C-1″), 133.77 (C-2″, 6″), 134.16 (C-5′), 135.15 (C-4′), 138.02 (C-4″).159.05 (C-2′), 167.52 (C-2),

Compound 4h. (Found N, 12.62 $C_{16}H_{13}N_3O_3S$ required N, 12.84) IR ($\nu_{max,}$ cm^{-1}): 3054 (S-H);^{1}H NMR (300 Hz; $CDCl_3$+DMSO-d_6) δ_H 3.82 (3H, s, OCH_3), 6.92–8.64 (9H, m, 5, 2′, 4′, 5′, 6′, 2″, 3″, 5″, 6″-H), 12.85 (1H, bs, S-H, exchangeable with D_2O);^{13}C NMR (75 Hz; $CDCl_3$+DMSO-d_6)δ_C 60.09 (OCH_3), 117.55 (C-5), 119.18 (C-3″, 5″), 124.85 (C-4), 125.62 (C-2′), 127.13 (C-4′), 131.00 (C-2″, 6″), 134.67 (C-6′), 134.96 (C-1″), 136.53 (C-5′), 143.62 (C-1′), 152.84 (C-3′), 164. 42 (C-4″), 168.04 (C-2).

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