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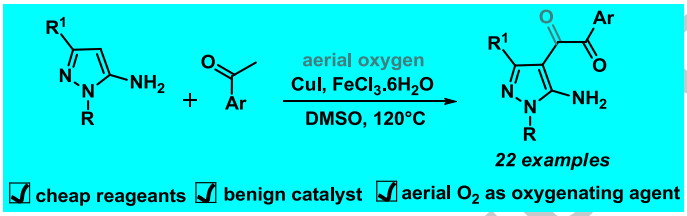

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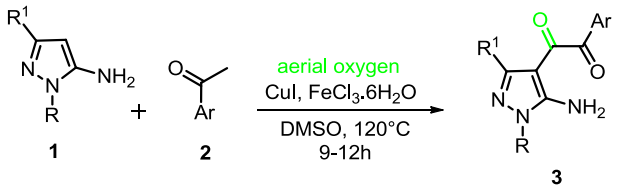
ABSTRACT

Cu(I)/Fe(III) promoted C4-dicarbonylation of 5-aminopyrazole is developed. The strategy involved radical triggered direct oxidative coupling of 5-aminopyrazoles with methyl ketones using aerial oxygen as a source of oxygen in newly generated carbonyl group. CuI is used as catalyst and $FeCl_3.6H_2O$ is used as additive and the reaction proceeded at 120 °C in DMSO for 9-12 h. It is found that use of Cu(II) catalyst gives the thiomethylated product by reacting with DMSO instead of oxidative coupling. A plausible mechanism is also given.

The importance of dicarbonyl compounds in organic synthesis cannot be overlooked. 1,2-Diketo derivatives are widely involved as intermediates in the synthesis of various natural products,[1] heterocycles,[2] and photosensitive agents.[3] Moreover, heterocycles containing 1,2-diketo moiety are a paramount class of medicinally active scaffolds. For example, terpestacin is an anti-cancer agent,[4] dolutegravir is HIV-1 integrase inhibitor.[5] On the other hand, interest in the chemistry of aminopyrazole has recently been revived.[6] This is because aminopyrazoles are the key components of many medicinally active compounds such as zaleplon, indiplon both of which function as hypnotics,[7] sulfaphenazole (antibacterial agent),[8] CDPPB (allosteric modulator),[9] ramifenazone (analgesic),[10] fipronil (insecticide),[11] allopurinol (used to treat gout and certain types of kidney stones, high blood uric acid level),[12] and Viagra (used to treat erectile dysfunction and pulmonary arterial hypertension).[13] Moreover, 5-aminopyrazoles are widely used synthetic precursor for the synthesis of various nitrogen containing heterocycles.[14]



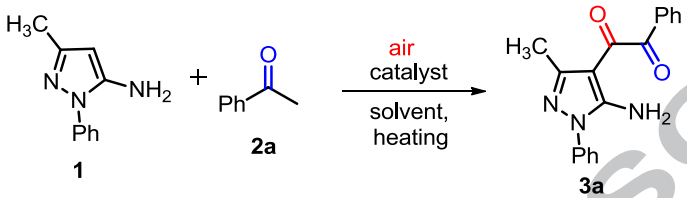
Scheme 1. C4 dicarbonylation of 5-aminopyrazole

C-H functionalization is an important field in organic synthesis over the last two decades for being more atom-economical, directive, and environmentally benign than other cross-coupling reactions which require additional steps for the prefunctionalization of substrates.[15] Few reports were available in the literature for the dicarbonylation of aromatic compounds through oxidative coupling with methyl ketones. Molecular iodine was employed in few cases for the dicarbonylation of indoles,[16] anilines[17] and amines.[18] Since many aminopyrazole derivatives are bioactive in nature, we planned to synthesize diverse 1,2-diketo compounds of pyrazol-5-amine by coupling with methyl ketones. Over the past few years our group explored many methodologies in which we maintained the green environment using atom and step economic reactions, non-hazardous metal/metal-free catalysis, cheap catalysts/substrates and solvent-free/environmentally benign solvents.[19] As non-hazardous molecular iodine helps such type of coupling,[16-18] we examined the feasibility of the present reaction by using I_2-TBHP in DMSO at 120 °C. However, we isolated 4-iodo-5-aminopyrazole (**4**) only and no dicarbonylation took place (Scheme 2). Here we disclose an easy and cost effective process for the dicarbonylation of 5-aminopyrazole by using Cu(I) in combination with Fe(III) in DMSO at 120 °C (Scheme 1). The main feature of this method is the involvement of aerial oxygen which works both as oxidant and oxygenating agent.

Initially, we carried out the reaction of 3-methyl-1-phenyl-1H-pyrazol-5-amine (**1**) with acetophenone (**2a**) in presence of various catalysts with or without additives in different solvents. As Cu(I) or Cu(II) can catalyse this type of reaction,[20] we used CuI and $Cu(OAc)_2$ as catalysts in our reaction under open air using DMSO as solvent. However, in both the cases we obtained thiomethylated product of 5-aminopyrazole **5** (entries 1-2, Table 1 and Scheme 2). We then used different additives along with copper catalysts. $FeCl_3$ (10 mol %) as additive along with $Cu(OAc)_2$ or other Cu(II) salts again furnished the

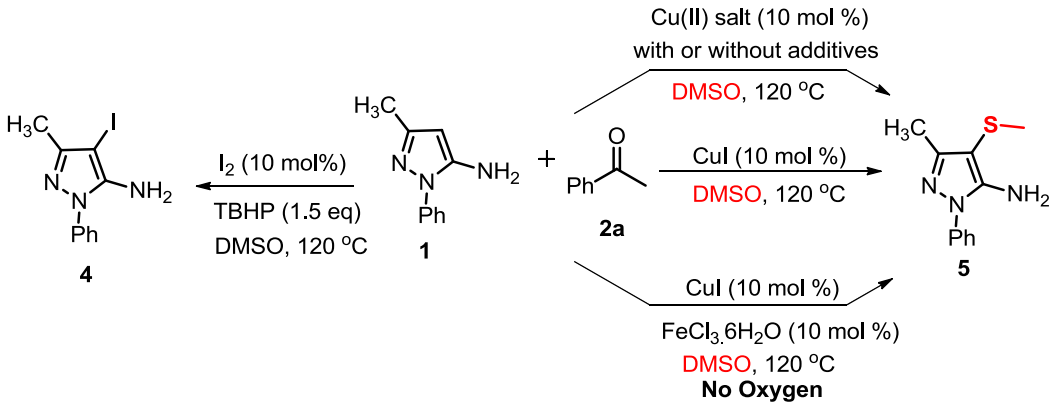
thiomethylated product (entries 3-5, Table 1). However, combination of CuI and $FeCl_3.6H_2O$ (10 mol % of each) gave us the desired dicarbonylated product **3a** (entry 6, Table 1). It was noticed that the presence of suitable additive is essential for the synthesis of **3**. We then used different additives such as $FeSO_4.7H_2O$, $BF_3.Et_2O$, Bronsted acids but did not improve the yield (entries 7-10, Table 1). Other Cu(I) catalysts such as CuBr, CuCl gave lower yield (entries 11-12, Table 1). We then screened different solvents for the reaction. However, except DMF other solvents were not suitable for the reaction (entries 13-16, Table 1). Use of increased amount of catalyst or additive in the reaction did not improve the product yield (entries 17-18, Table 1), but decreased amount of those affect the reaction yield (entries 19-20). Again the increase of reaction time and temperature did not help to obtain better yield (entries 21 & 23, Table 1). Without adding CuI the reaction failed to give the product (entry 25, Table 1). We found that aerial oxygen is essential for the reaction because in absence of oxygen C4-thiomethylation of **1** was observed (Scheme 2). Therefore, all the reactions were performed in an open reaction vessel.

Table 1. Optimization of the reaction for the synthesis of **3a**[a]



Entry	Catalyst (mol %)	Additive (mol %)	Solvent	Temp. (°C)	Time (h)	Yield[b] (%) 3a
1	$Cu(OAc)_2$ (10)	---	DMSO	120°C	12	---[c]
2	CuI (10)	---	DMSO	120°C	12	trace[c]
3	$Cu(OAc)_2$ (10)	$FeCl_3.6H_2O$ (10)	DMSO	120°C	12	---[c]
4	$Cu(OTf)_2$ (10)	$FeCl_3.6H_2O$ (10)	DMSO	120°C	12	---[c]
5	$CuSO_4.5H_2O$ (10)	$FeCl_3.6H_2O$ (10)	DMSO	120°C	12	---[c]
6	**CuI (10)**	**$FeCl_3.6H_2O$ (10)**	**DMSO**	**120°C**	**12**	**68**
7	CuI (10)	$FeSO_4.7H_2O$ (10)	DMSO	120°C	12	63
8	CuI (10)	$BF_3.Et_2O$ (10)	DMSO	120°C	12	55
9	CuI (10)	AcOH (10)	DMSO	120°C	12	Trace
10	CuI (10)	PTSA (10)	DMSO	120°C	12	Trace
11	CuBr (10)	$FeCl_3.6H_2O$ (10)	DMSO	120°C	12	32
12	CuCl (10)	$FeCl_3.6H_2O$ (10)	DMSO	120°C	12	25
13	CuI (10)	$FeCl_3.6H_2O$ (10)	DMF	120°C	12	55
14	CuI (10)	$FeCl_3.6H_2O$ (10)	toluene	reflux	12	Trace
15	CuI (10)	$FeCl_3.6H_2O$ (10)	CH_3CN	reflux	12	Trace
16	CuI (10)	$FeCl_3.6H_2O$ (10)	EtOH	reflux	12	Trace
17	CuI (15)	$FeCl_3.6H_2O$ (10)	DMSO	120°C	12	68
18	CuI (10)	$FeCl_3.6H_2O$ (15)	DMSO	120°C	12	66
19	CuI (5)	$FeCl_3.6H_2O$ (10)	DMSO	120°C	12	63
20	CuI (10)	$FeCl_3.6H_2O$ (5)	DMSO	120°C	12	61
21	CuI (10)	$FeCl_3.6H_2O$ (10)	DMSO	120°C	16	62
22	CuI (10)	$FeCl_3.6H_2O$ (10)	DMSO	120°C	10	64
23	CuI (10)	$FeCl_3.6H_2O$ (10)	DMSO	130°C	12	68
24	CuI (10)	$FeCl_3.6H_2O$ (10)	DMSO	110°C	12	60
25	---	$FeCl_3.6H_2O$ (10)	DMSO	120°C	12	---
26[d]	CuI (10)	$FeCl_3.6H_2O$ (10)	DMSO	120°C	12	---[c]

[a] Reaction conditions: **1** (1 mmol), **2a** (1.5 mmol), solvent (2 mL) under open air. [b] Isolated yields. [c] Thiomethylated product was isolated. [d] In absence of oxygen.



Scheme 2. Thiomethylation and iodination of 5-aminopyrazole

To establish the substrate scope and generality of the reaction, a variety of acetophenones were investigated under optimized reaction conditions and obtained good yield of **3** (Figure 1). It was found that electron withdrawing groups (-Cl, -Br, -F) attached on *para* position of acetophenone gave slightly better yield than electron donating groups (-Me, -OMe). However, functional groups attached on *meta* and *ortho* position did not affect the formation of product (**3g-k**, Figure 1). Good yields were also obtained in case of disubstituted acetophenones (**3l-m**, Figure 1). We have used heterocyclic methyl ketones which gave good yield of products (**3n-p**, Figure 1). Again use of 1-phenyl-1H-pyrazol-5-amine as substrate gave good yield (**3q**, Figure 1). Further replacing N-phenyl with C_6H_4(*p*-Cl) substituent in the pyrazole ring gave good yield of product (**3r**, Figure 1). Use of 1,3-dimethyl-1H-pyrazol-5-amine as substrate also afforded products with good yield (**3s-v**, Figure 1). However, reaction of aliphatic methyl ketones under optimal condition did not give desired product. Instead, we isolated the 4-formyl and 4-thiomethyl product of pyrazole-5-amine (**5** & **6**).

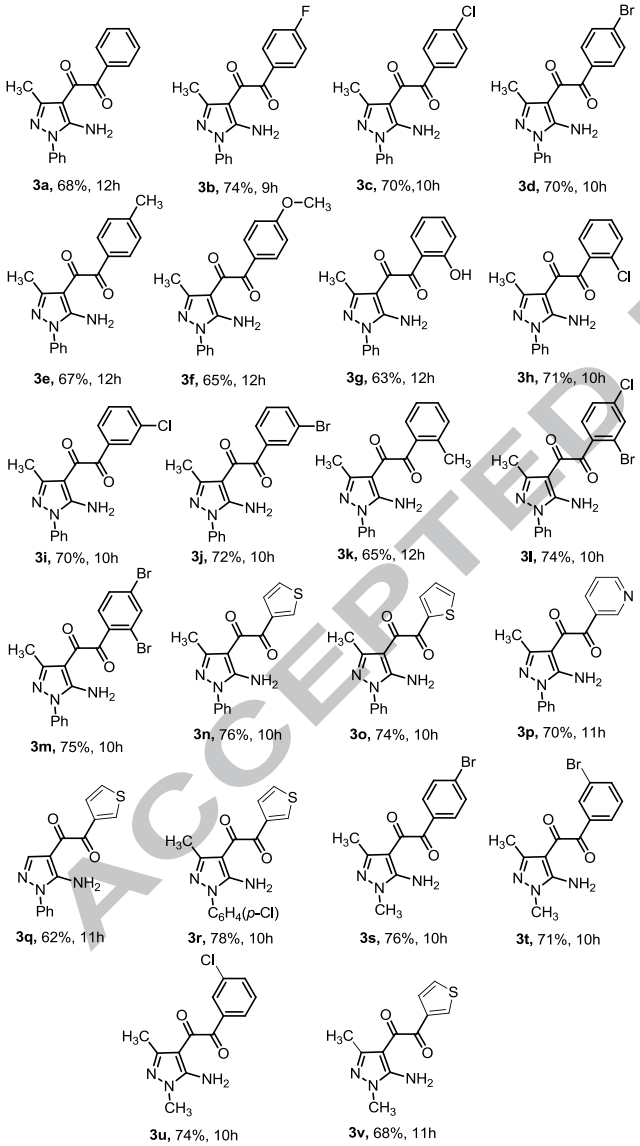
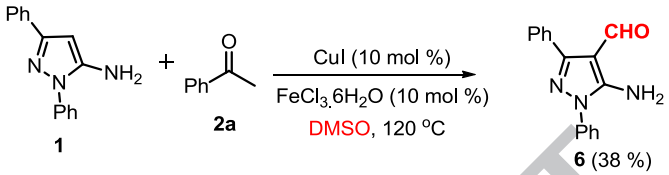


Figure 1. Synthesis of C4-dicarbonylated product of 5-aminopyrazole derivative

When we used 3-Phenyl substituted 5-aminopyrazole, surprisingly we obtained 4-formyl derivative of 5-aminopyrazole (Scheme 3). The different behaviour of this particular compound may be due to steric repulsion between phenyl group and incoming acetophenone. We assumed that the -CHO group must come from DMSO and therefore, we tested the above reaction in other solvents like toluene and *p*-xylene. However, no reaction took place. All the products obtained from the reaction were characterised by IR, NMR, mass spectra and single crystal X-ray analysis of compound **3c** (Figure 2).



Scheme 3. C4-Formylation of 3-phenyl substituted 5-aminopyrazole

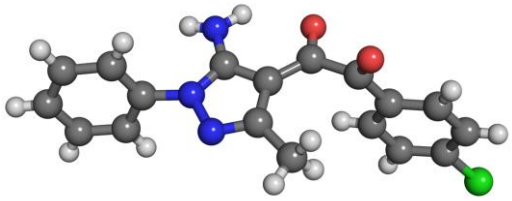
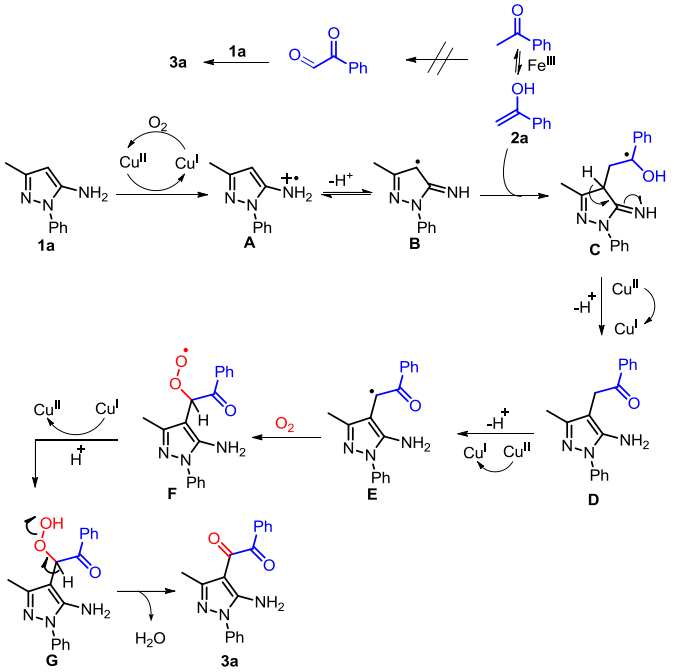


Figure 2. X-Ray structure of **3c** (CCDC No. 1887207)

To set up a mechanism for the reaction, we checked the reaction in presence of radical scavengers such as BHT and TEMPO (1.5 eq. each) under the optimal reaction condition. These scavengers almost fully prevented the reaction to occur. These results indicate a free radical route for the reaction. We also performed one reaction without adding aminopyrazole to check whether methylketone changes to diketone. However, no reaction was noticed which was confirmed by mass spectrometric analysis. Based on our observations and literature reports,[16-21] a tentative mechanism for the reaction is proposed (Scheme 4). Cu(I) is oxidized first to Cu(II) by aerial oxygen and then abstracts an electron from amine group of 5-aminopyrazole generating radical cation [**A**] which afterwards eliminates a proton to form radical imine [**B**]. We assume that the additive Fe(III) helps to tautomerize **2** to its enol form. Then the intermediate [**B**] adds to the enol form of **2** giving [**C**]. Intermediate [**C**] then successively eliminates two protons providing radical ketone [**E**]. This then reacts with molecular oxygen from air giving [**G**] *via* peroxy radical [**F**]. The hydroperoxide [**G**] finally removes a water molecule to produce the dicarbonylated product **3**. Though the active catalytic species in the reaction is Cu(II), despite that the



Scheme 4. Plausible mechanism for the reaction

reaction in presence of Cu(II) salt leads the formation of thiomethylated product (from the reaction of aminopyrazole and DMSO; Scheme 2).

Conclusions

In summary, we have developed a route to synthesize C4-dicarbonylated product of 5-aminopyrazole derivatives using a combination of Cu(I)/Fe(III) salts. All the reagents and catalysts are cheap and environmentally benign. Most importantly, aerial oxygen acts as oxygenating agent. We have also proposed a plausible mechanism for the reaction. Further investigation to uncover this type of transformation is under progress in our laboratory.

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Highlights

1. Dicarbonylation of aminopyrazole *via* oxidative C-H coupling.
2. Cu(I)/Fe(III) promoted reaction using aerial O_2 as oxygenating agent.
3. The reagents and catalysts are cheap and environmentally benign.
4. Broad substrate scope with 22 examples.