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An efficient solvent-free synthesis of *NH*-pyrazoles from β-dimethylaminovinylketones and hydrazine on grinding

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ABSTRACT

A series of *NH*-pyrazoles was efficiently synthesized from the reaction of β-dimethylaminovinylketones ($[R^1C(O)C(R^2)=CHN(Me_2)]$, where R^1 = Me, Ph, 3-MeO-Ph, 4-Me-Ph, 4-MeO-Ph, 4-F-Ph, 4-Cl-Ph, 4-Br-Ph, 4-O_2N-Ph, fur-2-yl, thien-2-yl; R^2 = H, 2-MeO-Ph; R^1, R^2 = $-(CH_2)_3C(O)-$) and hydrazine sulfate in solid state on grinding in the presence of *p*-toluenesulfonic acid (PTSA). Most of the reactions proceeded smoothly at room temperature under solvent-free conditions. In comparison with the classical reaction conditions, which employ molecular solvent (ethanol), this new synthetic method has the advantages of shorter times, higher yields, mild reaction conditions as well as being environmentally friendly.

At the beginning of the new century, interest in the development of economically simple and environmentally safe methods in synthetic organic chemistry is greater than ever. This interest is mostly apparent in the growth of 'Green Chemistry'. Green chemistry approaches not only offer significant potential to reduce by-products, waste produced, and energy costs but also in the development of new methodologies for previously unobtainable materials.[1] The perfectly 'green' reaction might be described as one which proceeds at room temperature, requires no organic solvent, is highly selective, and exhibits high atom efficiency, and yet produces no waste products.[2]

In recent years, solvent-free organic reactions[3] have captured great interest because of their many advantages such as high efficiency and selectivity, easy separation and purification, mild reaction conditions, reduction in waste, and benefit to the industry as well as the environment. Solvent-free organic reactions based on grinding two macroscopic particles together mostly involve the formation of a liquid phase prior to the reaction, that is, formation of a eutectic melt of uniform distribution where the reacting components being in proximity are poised to react in a controlled way.[4]

The grinding mode for solid-state reactions has been reported for Grignard reactions,[5] Reformatsky reactions,[6] Aldol condensations,[7] Dieckmann condensations,[8] Knoevenagel condensations,[9] reductions,[10] and others.[11] Most of these reactions are carried out at room temperature in an absolutely solvent-free environment using only a mortar and pestle. Exothermic reactions can be conducted by grinding the reactants together for a few minutes without using any organic solvent, nevertheless this method does not seem to be effective for endothermic reactions.[11d,e]

Synthesis of nitrogen-containing heterocyclic systems occupies an important place in the realm of natural and synthetic organic chemistry, due to their therapeutic and pharmacological properties.[12a] In particular, pyrazoles and their derivatives have attracted considerable attention due to their wide variety of biological activities, including anti-inflammatory, antipyretic, and analgesic activities,[12b,c] bactericides, fungicides,[12d–f] as well as promising inhibitory activity against monoamine oxidase for the treatment of diseases such as Parkinson's and Alzheimer's.[12g] The synthesis of pyrazoles has been well explored using the so-called [3+2] atom fragments, where 1,3-dielectrophilic compounds are used as 3-atom building blocks and hydrazines as the 2-atom fragment.[13]

Our research group has developed new synthetic methodologies for the synthesis of both building blocks and heterocyclic compounds based on the use of ultrasound irradiation,[14] microwave irradiation,[15] ionic liquids[16], and solvent-free conditions.[17,3a] Recently, we reported an efficient method to obtain a series of β-dimethylaminovinylketones (β-enaminones) from condensation of methyl ketones with dimethylformamide dimethylacetal (DMFDMA) in the presence of imidazolium-based ionic liquid [BMIM][BF_4].[16b] Thus, in continuation of our interest in the development of new methodologies, we describe herein the synthesis of a series of *NH*-pyrazoles from the reaction of β-dimethylaminovinylketones and hydrazine sulfate in solid state on grinding, using *p*-toluenesulfonic acid (PTSA) as a catalyst and solvent-free conditions. The β-dimethylaminovinylketones **1** used in this study were

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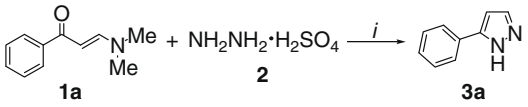
Table 1
Optimization for the synthesis of **3a**



i: grinding, r.t.

Entry	Catalyst	Catalyst amount (mol %)	Time (min)	Yield[a] (%)
1	Neat	—	6	—[b]
2	SiO_2	20	6	—[b]
3	SiO_2	100	6	—[b]
4	**PTSA**	**20**	**6**	**90**
5	PTSA	50	3	—[c]
6	PTSA	50	6	64
7	$KHSO_4$	20	6	—[d]
8	$NaHSO_4$	20	6	—[c]
9	$KHSO_4/SiO_2$	20	6	—[c]
10	$NaHSO_4/SiO_2$	20	6	—[c]
11	$PTSA/SiO_2$	20	6	—[c]

[a] Yield of isolated product.
[b] The starting material was recovered.
[c] A mixture of the starting material and pyrazole was obtained in a molar ratio of 1:1, respectively. This ratio was determined by ^1H NMR from the integration signal area of vinylic proton, and based on the consumption of compound **1**.
[d] A mixture of the pyrazole and the starting material was obtained in a molar ratio of 20:1, respectively (determined as in the item c).

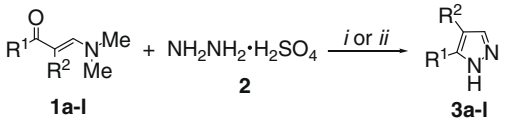
prepared according to the experimental procedures described previously in our laboratory.[16b,18]

We began our study by evaluating the efficiency of grinding in the reaction between β-dimethylaminovinylketone **1a** and hydrazine sulfate **2** in solid phase to obtain the pyrazole **3a** under the reaction conditions described in Table 1.

Initially, the mixture was ground in a mortar with a pestle at room temperature under neat conditions. However the results demonstrated the need of a catalyst, since the starting material was recovered (Table 1, entry 1). Thus, we chose four catalysts (SiO_2, PTSA, $KHSO_4$, and $NaHSO_4$) to be analyzed in this cyclocondensation reaction. The reaction failed in the presence of SiO_2 and **1a** was recovered (Table 1, entries 2 and 3). We found PTSA, an inexpensive and common organic chemical, to be an efficient catalyst for this reaction. PTSA was used in 20 mol %, which led to a yield improvement and completion of the reaction in 6 min (Table 1, entry 4). In order to evaluate the amount of catalyst, PTSA was employed in 50 mol % for 3 and 6 min, however in the first case compound **1a** was partially recovered together with product **3a**, while the second attempt led to a yield decrease (Table 1, entries 5 and 6). A mixture of the pyrazole and the starting material was obtained in a molar ratio of 20:1, respectively, when $KHSO_4$ was used and 1:1 when $NaHSO_4$ was used (Table 1, entries 7 and 8). The efficiency of solid-acid catalysts on the solid support SiO_2 was also investigated, and the results revealed the conversion of only half of the starting material to the desired product (Table 1, entries 9–11). Another parameter evaluated was the amount of hydrazine used. It was observed that the molar ratio of 1:1.2 (β-enaminone/hydrazine) was enough for the total conversion of the starting material. These data demonstrate that the cyclocondensation reaction between **1a** and hydrazine **2** can be performed under mild conditions. During the optimization reactions using PTSA, it was observed that the reaction mixture, which was initially in a solid state, melted during the grinding process leading to a light yellow solid mass. The product was extracted from the solid mass furnishing 5-phenyl-1*H*-pyrazole **3a** in excellent yield (90%).

In order to evaluate the scope and limitations of this solvent-free reaction, we extended it to β-enaminones **1b–l**, using the same reaction conditions that were established for **1a**. The mixture was ground with a pestle, and the reaction was completed within 6–12 min in good yields (Table 2).[19] From Table 2, it is possible to affirm that the grinding allowed the reaction to proceed in a shorter reaction time, furnishing better yields when compared to conventional thermal heating, with ethanol reflux and a Brønsted catalyst (PTSA). A possible explanation for the shorter reaction time and better yield under solvent-free conditions is that the formation of a liquid phase prior to the reaction, that is, formation of a eutectic mixture with uniform distribution of the reactants, brings the

Table 2
Solvent-free reactions of solid β-enaminones **1a–l** with hydrazine **2**



i: PTSA, grinding, r.t.
ii: PTSA, ethanol, reflux

Product	R^1	R^2	Grinding			Ethanol reflux	
			Time (min)	Conv.[a] (%)	Yield[b] (%)	Time (h)	Yield[b] (%)
3a	Ph	H	6	>99	90	2	79
3b	3-MeO-Ph	H	6	>99	84	3	81
3c	4-Me-Ph	H	6	>99	75	3	66
3d	4-MeO-Ph	H	6	>99	91	3	74
3e	4-F-Ph	H	6	>99	72	3	72
3f	4-Cl-Ph	H	9	95	84	4	83
3g	4-Br-Ph	H	6	>99	85	3	80
3h	$4\text{-}O_2N\text{-}Ph$	H	12	91	75	6	69
3i	Fur-2-yl	H	6	>99	65	3	51
3j	Thien-2-yl	H	6	>99	75	3	67
3k	Me	2-MeO-Ph	6	>99	92	3	75
3l	$-(CH_2)_3C(O)-$		6	97	60	3	50

[a] Determined by ^1H NMR from the integration signal area of vinylic proton, and based on the consumption of compound **1**.
[b] Yield of isolated products.

Table 3
Results obtained using large-scale synthesis (Grindstone Chemistry)

Entry	Product	R^1	β-Enaminone amount (mmol)	Time (min)	Yield[a] (%)
1	**3a**	Ph	25	6	90
2	**3a**	Ph	50	6	92
3	**3c**	4-Me-Ph	25	6	89
4	**3e**	4-F-Ph	25	6	84

[a] Yield of isolated products.

reacting species into proximity than does a solvent.[20] In addition, this implies that some heat is released upon the grinding of the two components which leads to complete melting of the mixture. Such heat may be generated by the occurrence of 'hot spots' during initial grinding of the solids.[1,2,4]

All the reactions proceeded smoothly until completion at room temperature. The conversion of starting material into the respective products was determined by ^{1}H NMR from the integration signal area of vinylic proton, and based on the consumption of β-enaminones **1**, as demonstrated in Table 2. It is important to mention that the conversion was 100% for most compounds, except for compounds **3f**, **3h**, and **3l**, where small amounts of the starting material were observed. The substituent effect on the aromatic ring in **1b**–**h** was also evaluated. As shown in Table 2, compounds **1b**–**g** containing electron-donating groups (such as alkyl group) or weak electron-withdrawing groups (such as halides) reacted well to give the corresponding **3b**–**g** in high yields. This finding demonstrated no influence of the electronic nature of the substituent on the reaction time, except for the 4-Cl-Ph group, which required a longer reaction time (9 min). On the other hand, when a strong electron-withdrawing group (4-O_2N-Ph) was used, a longer time (12 min) was necessary to obtain product **3h**. The smaller reactivity of **1h** in relation to **1a** can be explained in terms of substituent (R^1) effect on the electrophilicity of C-1 (C═O) and/or C-3 (carbon-β). From the semi-empirical AM1 calculation data,[21] it was observed that the charge density and the LUMO coefficient values of C-1 and C-3 for **1h** (R^1 = 4-O_2N-Ph) are close to half of those observed for the β-enaminone **1a** (R^1 = Ph). Also, the charge density of C-1 atom for **1h** indicates that there is a π-electron delocalization toward the nitro group, which led to the increasing of the double bond character on the carbonyl group. In addition, we observed that the substituent position in the benzene ring had no effect on the product yield.

The reaction of hydrazine with **1** containing R^1 with π-excedent heterocycles (fur-2-yl and thien-2-yl) as substituent groups was also performed. The desired products were obtained in low reaction time and good yields.

In order to demonstrate the efficiency and reproducibility of this new synthetic approach for obtaining *NH*-pyrazoles, the reactions between **1** and **2** were performed at least three times and the average yield presented a standard deviation of ±2%.

The spectroscopic data of the compounds synthesized herein are in accordance with the literature.[22]

Recently, the technique 'Grindstone Chemistry' has been reported as an efficient way for the synthesis of organic compounds in large scale.[23,11d,e] This method was developed especially for solvent-free reactions activated by grinding solid reactants together. To support this process, we investigated the efficiency of our procedure using the β-enaminones **1a,c,e** and hydrazine **2** (Table 3). For this purpose we chose three representative β-enaminones containing in their structure hydrogen, electron-donating groups and weak electron-withdrawing groups. The reactions were performed in a mortar and pestle at room temperature and the reactants were used in the same ratio as previously determined. Thus, a large-scale synthesis of compound **3a** was carried out on 25 and 50 mmol scale (Table 3, entries 1 and 2). The reaction mixture was ground for just few minutes and the desired product was obtained in 90% and 92% yield, respectively. Similar results were attained for β-enaminones **1c** and **1e** (Table 3, entries 3 and 4).

In summary, this Letter describes an efficient and practical solvent-free process for the synthesis of *NH*-pyrazoles in both small and large scale. Furthermore, the procedure described herein offers several advantages including high yields, clean product, and minimal environmental impact. The short reaction time coupled with the simplicity of the reaction procedure makes this method one of the most efficient methods for the synthesis of this class of compounds.

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Supplementary data

Supplementary data (general procedures and characterization data (^{1}H NMR, ^{13}C NMR, GC/MS and melting points) of compounds **3a**–**l**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.04.038.

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19. *General procedure for the preparation of NH-pyrazole 3a: (a) Reactions on grinding:* A mixture of the appropriate solid β-enaminone **1a** (1 mmol), hydrazine sulfate **2** (1.2 mmol), and *p*-toluenesulfonic acid (20 mol %) was ground in a mortar and pestle at room temperature for the appropriate time. After completion of the reaction, water was added and the product was extracted with $CHCl_3$ (2 × 3 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to give a product **3a** with high purity.
(b) *Reactions in ethanol:* Powdered reactants **1a** and **2** were dissolved in ethanol, and *p*-toluenesulfonic acid (20 mol %) was added. The reaction mixture was stirred in ethanol under reflux during 2 h. After completion of the reaction, ethanol was removed under reduced pressure. Water was added and the product was extracted with $CHCl_3$ (2 × 3 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to give the product **3a** with high purity. Typical spectral data are as follows: *5(3)-Phenyl-1H-pyrazole* (**3a**): mp 69–71 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ_H (ppm) 6.58 (d, ^3J = 2 Hz, 1H, H4), 7.26–7.42 (m, 3H, Ar), 7.58 (d, ^3J = 2 Hz, 1H, H3), 7.73–7.72 (m, 2H, Ar), 10.12 (br s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ_C (ppm) 102.5 (C4), 125.8, 127.9, 128.7, 132.1 (C-Ar), 134.4 (C5), 149.0 (C3); GC/MS (*m/z*, %) 144 (M^+, 100), 115 (20), 77 (12), 63 (7), 51 (6).
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