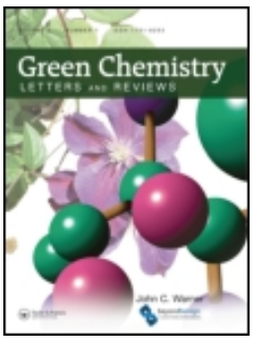

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RESEARCH LETTER

An atom efficient, green synthesis of 2-pyrazoline derivatives under solvent-free conditions using grinding technique

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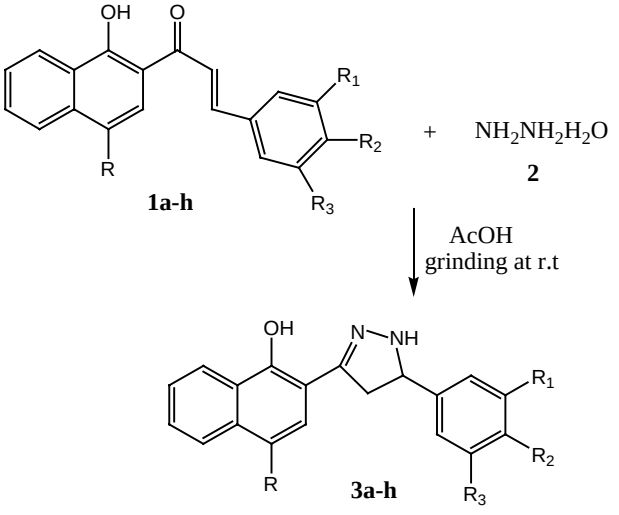
A simple, rapid, efficient, and environmentally benign procedure for synthesis of 2-pyrazoline derivatives has been achieved by reacting 2′-hydroxychalcones with hydrazine hydrate under solvent-free grinding technique. The short reaction time, cleaner reaction, easy workup, higher yields, and mild reaction conditions make this protocol practical and economically attractive in comparison with the classical reaction.



Keywords: 2′-hydroxychalcones; 2-pyrazolines; solvent free; grinding technique; green chemistry

Introduction

Solid-state reaction without using harmful organic solvent has captured great current interest especially in the development of green chemistry (*1–4*) and its applications in synthetic organic chemistry (*5–9*). In view of these observations in recent years, environmentally benign synthetic methods have received considerable attention, and some solvent-free protocols have been developed (*10, 11*). Grinding technique is one which has been increasingly used in organic synthesis compared to traditional methods (*12, 13*). These reactions not only of interest from economical point of view, but also in many cases they offer considerable advantages in terms of yield, selectivity, and simplicity of reaction procedure with high atom efficiency.

The grinding mode for solid-state reactions has been reported for some well-known reactions such as Grignard reactions (*14*), Reformatsky reactions (*15*), Aldol condensations (*16*), Dieckmann condensations (*17*), Knoevenagel condensations (*18*), Reductions (*19*), and others (*20, 21*). Most of these reactions are carried out at room temperature in absence of solvent-free environment, using only a mortar and pestle. In grindstone technique, reaction occurs through generation of local heat by grinding of crystals of substrate and reagent. Reactions are initiated by grinding, with the transfer of very small amount of energy through friction. In some cases, a mixture and reagent turn to a glassy material. Such reactions are simple to handle, reduce pollution, comparatively cheaper to operate and may regarded

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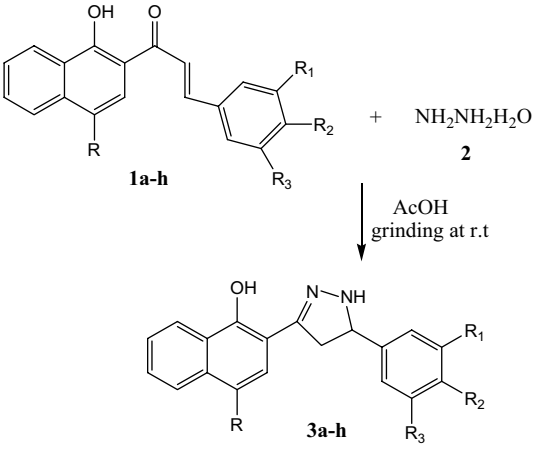
as more economical and ecologically favorable procedure in chemistry (*22*).

Amongst five-membered heterocycles, pyrazolines represent a class of compounds of great importance in heterocyclic chemistry (*23, 24*). These compounds have intrinsic biological activities and constitute the structural feature of many bioactive compounds. Pyrazolines are known for their pronounced biological activities (*25–34*). A classical synthesis of these compounds involves the condensation of α,β-unsaturated carbonyl compounds with hydrazines (*35*). Pyrazoline is also synthesized by using microwave irradiation and ultrasound irradiation (*36, 37*). Recently, various modified methods have been reported for synthesis of 2-pyrazolines by using different catalysts such as $KHSO_4H_2O/SiO_2$ (*38*), porous calcium hydroxyappatite (*39*), mercuric acetate (*40*), $Bi(NO_3)_3{\cdot}5H_2O$ (*41*), Zn (*42*), $H_3PW_{12}O_{40}$ (*43*), and Lewis acid/Lewis bases (*44*). The combination of solvents, costly chemicals/catalyst, and long reaction time make these methods environmentally hazardous. To improve these methods toward organic synthesis and reactions, increasing attention is being focused on green chemistry using environmentally benign reagents and conditions, particularly solvent-free procedures. Thus, utilization of nontoxic chemicals, renewable materials, and solvent-free conditions is the key issue of green synthetic strategy. In view of these observations, it was thought worthwhile to synthesize 2-pyrazoline derivatives from α,β-unsaturated carbonyl compounds by using grinding technique as it meets the requirement of greenness.

Results and discussion

In continuation of earlier research work on organic synthesis (*45–50*), we wish to report herein, a simple, rapid, and highly efficient procedure for the synthesis of 2-pyrazoline derivatives **3a–h** using catalytic amount of acetic acid under solvent-free grinding technique (Scheme 1). A variety of methods have been reported for the preparation of this class of compounds. However, in spite of their potential utility, some of the reported methods suffer from drawback such as long reaction time, cumbersome product isolation procedure, and environmental concerns.

The present studies describe that reactions were carried out using grindstone technique simply by mixing corresponding 2′-hydroxychalcones **1a–h** and hydrazine hydrate **2**. The mixture was ground together in mortar with pestle at room temperature for 2–3 minutes, and then a catalytic amount of acetic acid was added to this grinded reaction mixture. The grinding was continued for 8–12 minutes and progress of



Scheme 1. Synthesis of 2-pyrazoline derivatives under solvent-free conditions using grinding technique.

reaction was monitored on Thin layer chromatography (TLC). The completion of reaction was indicated by wetting with the formation of light greenish-colored reaction mixture. Obtained solid was easily separated by using cold water and simple Buchner filtration; final purification was achieved by crystallization from ethanol. The present method reported here for synthesis of 2-pyrazoline derivatives **3a–h** is simple and effective in terms of short reaction time, excellent yields, and simple reaction procedure with high atom efficiency. It is also consistent with green chemistry approach because it does not require heating or microwave irradiation. It occurs at room temperature and is completely free from organic solvents during both the reaction and separation of the product, except for recrystallization of product **3a–h**.

All newly synthesized compounds **3a–h** were established on the basis of spectral and elemental analysis. In IR spectra of condensed products, compounds **3a–h** display disappearance of band at 1625–1635 cm^{-1} due to C = O of 2′-hydroxychalcone and appearance of a band near 1590 cm^{-1} due to C = N formed. The band at near 3320 cm^{-1} revealed the presence of N–H stretching. The ^1H NMR spectra showing an ABX pattern were observed; H_A, H_B, and H_X appear as pair of doublets near δ 3.24, 3.76, and 4.90 ppm with $J_{AB} = 17.6$ Hz, $J_{AX} = 5.2$ Hz, $J_{BX} = 12.1$ Hz. The chemical shift for aromatic protons was observed at δ 7.25–8.20 ppm and that of N–H pyrazolo at δ 6.90 ppm.

Experimental

Melting points are uncorrected and determined in an open capillary tube. IR spectra were recorded on FTIR Shimadzu spectrometer. ^1H NMR spectra were recorded in DMSO-d_6 on Avance 300 MHz spectrometer

using Tetramethylsilane (TMS) as an internal standard. The mass spectra were recorded on EI-Shimadzu-GC–MS spectrometer. Elemental analyses were performed on a Carlo Erba 106 perkin-Elmer model 240 analyzer.

Typical procedure for synthesis of 2-pyrazoline derivatives

A mixture of 2′-hydroxychalcone **1a–h** (0.01 mol) and hydrazine hydrate **2** (0.02 mol) was thoroughly ground with a pestle in an open mortar at room temperature for 2–3 minutes. Acetic acid (0.001 mmol) was added to this reaction mixture and grinding continued for several minutes (Table 1). On completion of reaction as monitored by TLC, the light greenish-colored solid was separated out. The obtained solid was diluted with cold water and isolated by simple Buchner filtration and recrystallized from ethanol to give 2-pyrazoline derivatives **3a–h**. The physical data of newly synthesized compounds are reported in Table 1.

2-[5-(3,4,5-Trimethoxy-phenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-naphthalen-1-ol (a): IR (ν max) cm^{-1}: 3313 (N–H), 1589 (C = N). ^{1}H NMR (300 MHz, DMSO) δ 3.42 (s, 6*H*, OCH_3), δ 3.80 (s, 3*H*, OCH_3), δ 3.26 (dd, $J = 5.2$, 17.8 Hz, 1*H*, H_A), δ 3.78 (dd, $J = 12.1$, 17.8 Hz, 1*H*, H_B), δ 4.90 (dd, $J = 5.1$, 12.0 Hz, 1*H*, H_X), δ 6.71 (s, 1*H*, N–H), δ 7.32–8.21 (m, 8*H*, Ar–H), δ 12.2 (s, 1*H*, OH). ^{13}C NMR (DMSO) 148 (C = N), 138–112 (=CH, Ph), 49.52 (−CH), 40.78 (−CH_2), 52.28 (−OCH_3). MS *m*/*z*: 378 (M^+). Anal. Calc. for $C_{22}H_{22}O_4N_2$: C, 69.84; H, 5.82. Found: C, 69.81; H, 5.84.

4-Iodo-2-[5-(3,4,5-trimethoxy-phenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-naphthalen-1-ol (b): IR (ν max) cm^{-1}: 3321 (N–H), 1591 (C = N). ^{1}H NMR (300 MHz, DMSO) δ 3.46 (s, 6*H*, OCH_3), δ 3.81 (s, 3*H*, OCH_3), δ 3.22 (dd, $J = 5.1$, 17.6 Hz, 1*H*, H_A), δ 3.79 (dd, $J = 12.0$, 17.8 Hz, 1*H*, H_B), δ 4.92 (dd, $J = 5.0$, 12.1 Hz, 1*H*, H_X), δ 6.75 (s, 1*H*, N–H), δ 7.28–8.16 (m, 7*H*, Ar–H), δ 12.0 (s, 1*H*, OH). ^{13}C NMR (DMSO) 151 (C = N), 140–112 (=CH, Ph), 49.76 (−CH), 40.81 (−CH_2), 52.37 (−OCH_3). MS *m*/*z*: 504 (M^+). Anal. Calc. for $C_{22}H_{21}O_4N_2I$: C, 52.38; H, 4.16; X (I), 25.19. Found: C, 52.40; H, 4.18; X (I), 25.22.

2-[5-(3,4-Dimethoxy-phenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-naphthalen-1-ol (c): IR (ν max) cm^{-1}: 3318 (N–H), 1594 (C = N). ^{1}H NMR (300 MHz, DMSO) δ 3.42 (s, 6*H*, OCH_3), δ 3.20 (dd, $J = 5.0$, 17.4 Hz, 1*H*, H_A), δ 3.75 (dd, $J = 11.9$, 17.6 Hz, 1*H*, H_B), δ 4.90 (dd, $J = 5.0$, 12.0 Hz, 1*H*, H_X), ‘ 6.78 (s, 1*H*, N–H), δ 7.24–8.21 (m, 9*H*, Ar–H), 12.2 (s, 1*H*, OH). ^{13}C NMR (DMSO) 148 (C = N), 137–110 (=CH, Ph), 48.65 (−CH), 40.32 (−CH_2), 52.44 (−OCH_3). MS *m*/*z*: 348 (M^+). Anal. Calc. for $C_{21}H_{20}O_3N_2$: C, 72.41; H, 5.74. Found: C, 72.38; H, 5.76.

2-[5-(4-Chloro-phenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-naphthalen-1-ol (d): IR (ν max) cm^{-1}: 3324 (N–H), 1588 (C = N). ^{1}H NMR (300 MHz, DMSO) δ 3.24 (dd, $J = 5.2$, 17.6 Hz, 1*H*, H_A), δ 3.78 (dd, $J = 12.2$, 17.6 Hz, 1*H*, H_B), δ 4.92 (dd, $J = 5.1$, 12.1 Hz, 1*H*, H_X), δ 6.81 (s, 1*H*, N–H), δ 7.28–8.25 (m, 10H, Ar–H), 12.4 (s, 1*H*, OH). ^{13}C NMR (DMSO) 150 (C = N), 141–114 (=CH, Ph), 48.82 (−CH), 40.38 (−CH_2). MS *m*/*z*: 322 (M^+). Anal. Calc. for $C_{19}H_{15}N_2OCl$: C, 70.80; H, 4.65; X (Cl), 11.02. Found: C, 70.83; H, 4.67; X (Cl), 11.08.

2-[5-(4-Chloro-phenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-4-iodo-naphthalen-1-ol (e): IR (ν max) cm^{-1}: 3326 (N–H), 1590 (C = N). ^{1}H NMR (300 MHz, DMSO) δ 3.26 (dd, $J = 5.2$, 17.8 Hz, 1*H*, H_A), δ 3.81 (dd, $J = 12.2$, 17.8 Hz, 1*H*, H_B), δ 4.91 (dd, $J = 5.1$, 12.1 Hz, 1*H*, H_X), δ 6.82 (s, 1*H*, N–H), δ 7.26–8.23 (m, 9*H*, Ar–H), 12.2 (s, 1*H*, OH). ^{13}C NMR (DMSO)

Table 1. Synthesis of 2-pyrazoline derivatives under solvent-free conditions using grinding technique.

					Grinding[a]		
Product	R	R_1	R_2	R_3	Time (min)[b]	Melting point (°C)	Yield (%)
3a	H	OCH_3	OCH_3	OCH_3	8	190–192	94
3b	I	OCH_3	OCH_3	OCH_3	6	147	88
3c	H	OCH_3	OCH_3	H	9	174–176	92
3d	H	H	Cl	H	6	182	83
3e	I	H	Cl	H	5	178	89
3f	I	OCH_3	OCH_3	H	7	164	84
3g	Br	OCH_3	OCH_3	OCH_3	10	152	91
3h	H	H	F	H	12	146–148	78

[a]Under solvent-free condition
[b]Time required for conversion of reactants into product.

148 (C = N), 141–110 (=CH, Ph), 48.76 (−CH), 40.35 ($-CH_2$). MS *m/z*: 448 (M^+). Anal. Calc. for $C_{19}H_{14}N_2OICl$: C, 50.89; H, 3.12; X (I + Cl), 36.16. Found: C, 50.87; H, 3.10; X (I + Cl), 36.12.

2-[5-(3,4-Dimethoxy-phenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-4-iodo-naphthalen-1-ol (f): IR (*v* max) cm^{-1}: 3319 (N–H), 1592 (C = N). ^1H NMR (300 MHz, DMSO) δ 3.40 (s, 6*H*, OCH_3), δ 3.21 (dd, $J = 5.0$, 17.5 Hz, 1*H*, H_A), δ 3.77 (dd, $J = 12.0$, 17.6 Hz, 1*H*, H_B), δ 4.92 (dd, $J = 5.0$, 12.0 Hz, 1*H*, H_X), δ 6.78 (s, 1*H*, N–H), δ 7.22–8.23 (m, 8*H*, Ar–H), 12.2 (s, 1*H*, OH). ^{13}C NMR (DMSO) 146 (C = N), 139–112 (=CH, Ph), 48.62 (−CH), 40.35 ($-CH_2$), 52.42 ($-OCH_3$). MS *m/z*: 474 (M^+). Anal. Calc. for $C_{21}H_{19}O_3N_2I$: C, 53.16; H, 4.00; X (I), 26.73. Found: C, 50.39; H, 4.28; X (I), 26.75.

4-Bromo-2-[5-(4-methoxy-phenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-naphthalen-1-ol (g): IR (*v* max) cm^{-1}: 3323 (N–H), 1587 (C = N). ^1H NMR (300 MHz, DMSO) δ 3.48 (s, 3*H*, OCH_3), δ 3.23 (dd, $J = 5.1$, 17.6 Hz, 1*H*, H_A), δ 3.79 (dd, $J = 12.1$, 17.6 Hz, 1*H*, H_B), δ 4.88 (dd, $J = 5.0$, 12.0 Hz, 1*H*, H_X), δ 6.75 (s, 1*H*, N–H), δ 7.17–8.12 (m, 9*H*, Ar–H), 12.0 (s, 1*H*, OH). ^{13}C NMR (DMSO) 148 (C = N), 135–112 (=CH, Ph), 48.71 (−CH), 40.39 ($-CH_2$), 52.48 ($-OCH_3$). MS *m/z*: 397 (M^+). Anal. Calc. for $C_{20}H_{17}O_2N_2Br$: C, 50.37; H, 4.28; X (Br), 20.15. Found: C, 50.39; H, 4.29; X (Br), 20.17.

2-[5-(4-Fluoro-phenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-naphthalen-1-ol (h): IR (*v* max) cm^{-1}: 3324 (N–H), 1588 (C = N). ^1H NMR (300 MHz, DMSO) δ 3.26 (dd, $J = 5.2$, 17.8 Hz, 1*H*, H_A), δ 3.80 (dd, $J = 12.2$, 17.8 Hz, 1*H*, H_B), δ 4.94 (dd, $J = 5.1$, 12.1 Hz, 1*H*, H_X), δ 6.82 (s, 1*H*, N–H), δ 7.25–8.25 (m, 10*H*, Ar–H), 12.4 (s, 1*H*, OH). Anal. Calc. for $C_{19}H_{15}N_2OF$: C, 74.50; H, 4.90; X (F), 6.20. Found: C, 74.48; H, 4.88; X (F), 6.17.

Conclusion

In summary, we have developed a novel, simple, highly atom-efficient, economical, and environmentally benign protocol toward the synthesis of 2-pyrazolines by grinding under solvent-free conditions.

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