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Green and Effective One-Pot Synthesis of 5-Oxo-pyrazolidine and 5-Amino-2,3-dihydro-1*H*-Pyrazole Derivatives through Ball Milling Under Catalyst-Free and Solvent-Free Conditions

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A high-yield synthesis method for the one-pot synthesis of new 5-oxo-pyrazolidine and 5-amino-2,3-dihydro-1*H*-pyrazole derivatives was developed using ball milling under solvent-free and catalyst-free conditions. The proposed method is simple, economical and eco-friendly.

Keywords: Ball milling, Solvent-free, Catalyst-free, One-pot synthesis, 5-Oxo-pyrazolidine, 5-Aminopyrazole.

INTRODUCTION

Ball milling is a mechanical technique extensively used for grinding to obtain powders with fine particles [1-4]. In conventional methods, reactants are broken apart by solvent molecules. By contrast, reactants are broken apart using mechanical forces in ball milling, resulting in an amorphous mixture of all reagents and a large surface area for the reaction. Solvent-free ball milling has been rarely applied in organic synthesis. Nevertheless, this technique has gained considerable attention because of its simplicity, low cost and environment friendliness and its capability to achieve high yields.

The applications of ball milling in organic synthesis [5-11] have permitted other investigators to synthesize different types of organic compounds; these applications include preparation of phosphorus ylides [12], functionalization of Knoevenagel condensations [13], synthesis of functionalized indan-1,3-diones [14], coordination polymers [15], synthesis of nitrones [16], reductive benzylation of malononitrile [17], protection of diols/diamines [18], functionalization of fullerenes [19], Heck-type reactions [20,21], aldol reaction [22,23], Suzoku-type reaction [24-27], pyrano pyrimidine-dione synthesise [28], symmetrical and unsymmetrical thioureas [29] and functionalized 2-amino-3-cyano-4*H*-pyrans [30]. Moreover, different reactions in organic chemistry using ball milling have been reviewed [31-34].

Pyrazolidine and pyrazole derivatives are of great interest to researchers because they generally exhibit diverse biological properties, such as analgesic [35-37], antimycobacterial [38,39], antibacterial [40,41], antifungal [42,43], anti-inflammatory [44,45], antihypertensive [46], anti-HIV [47,48], antitumor [49-54], gastric secretion stimulatory [55], antidepressant [56] and antifilarial activities [57,58].

The synthesis of pyrazolidine and pyrazole derivatives [59-62] is generally performed under traditional conditions with different catalysts, solvents and elevated temperatures. Recently, Martins *et al*. [63] and Zhang *et al*. [64] described the synthesis of some pyrazoles by ball milling technique and using catalysts, however this study investigates one-pot three component synthesis of 5-oxo-pyrazolidine and 5-amino-2,3-dihydro-1*H*-pyrazole derivatives through simple ball milling without adding any catalyst and solvent to obtain high yields.

EXPERIMENTAL

The ball mill used in this study was an SPEX 8000 mixer with 10 cm^3 stainless steel vials. Melting points were determined using a Stuart Melting point apparatus SMP10. IR spectra were obtained with an FT-IR-Tensor 27 spectrometer in KBr pellets. ^1H NMR and ^{13}C NMR spectra were determined with a BRUKER 500 NMR spectrometer in DMSO-d_6 with TMS as internal standard. Chemical shifts are expressed as δ ppm units. Elemental analysis was carried out on a Perkin Elmer 2400 CHN elemental analyzer. The progress of all reactions was monitored through TLC on silica gel 60 (Merck) using chloroform-ethanol.

General procedure for the synthesis of pyrazolidine compound 4a (*cis*/*trans*): An equimolar amount (0.02 mol) of benzaldehyde, phenylhydrazine and malonic acid was placed into stainless steel vials with 31.80 g of stainless steel

balls (12 mm in diameter). The vials was closed then placed in an SPEX 8000 mixer. The pure form of compound **4a** was obtained after 60 min of milling without further purification as an inseparable mixture of diastereomers.

(*cis/trans*) 5-Oxo-1,3-diphenyl-pyrazolidine-4-carboxylic acid (4a): m.p.: 135-136 °C; IR (KBr, ν_{max}, cm^{-1}): 3270.93, 3023.91, 2953.91, 1697.84, 1683.98, 1591.00, 1493.23; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.61 (br, s, 2xNH, 2xOH, 4H), 8.11-7.15 (m, Ar, 20H), 5.18 (d, CH, 1H, J^3 = 7.90 Hz), 5.14 (d, CH, 1H, J^3 = 8.85 Hz), 3.61-3.58 (m, 2xCH, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 173.24, 173.21, 169.25, 166.12, 138.78, 137.92, 135.31, 128.15, 127.70, 127.45, 127.14, 123.46, 118.98, 63.18, 54.75; Anal. calcd. (%) for $C_{16}H_{14}N_2O_3$ (282.30): C, 68.08; H, 5.00; N, 9.92. Found (%): C, 68.12; H, 4.95; N, 9.91.

(*cis/trans*) 3-(4-Methoxy-phenyl)-5-oxo-1-phenyl-pyrazolidine-4-carboxylic acid (4b): m.p.: 114-115 °C; IR (KBr, ν_{max}, cm^{-1}): 3273.76, 3023.33, 2952.49, 1697.42, 1678.31, 1595.25, 1497.49; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.62 (br, s, 2xNH, 2xOH, 4H), 8.02-6.75 (m, Ar, 18H). 5.15-5.12 (m, 2xCH, 2H), 3.74 (s, 2xCH_3, 6H), 3,71-3.68 (m, 2xCH, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 173.62, 173.29, 169.81, 165.73, 159.13, 139.33, 129.16, 128.62, 126.11, 119.27, 113.66, 64.07, 55.34, 54.85; Anal. calcd. (%) for $C_{17}H_{16}N_2O_4$ (312.33): C, 65.38; H, 5.16; N, 8.97. Found (%): C, 65.36; H, 5.14; N, 9.01.

(*cis/trans*) 1-(2,4-Dinitro-phenyl)-5-oxo-3-phenyl-pyrazolidine-4-carboxylic acid (4c): m.p.: 220-221 °C; IR (KBr, ν_{max}, cm^{-1}): 3282.59, 3080.00, 2915.22, 1705.22, 1680.25, 1582.50, 1495.33; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.86 (m, 2xCHarom, 2H), 8.63 (br, s, 2xNH, 2xOH, 4H), 8.46-7.20 (m, Ar, 14H), 5.14-5.12 (m, 2xCH, 2H), 3.73-68 (m, 2xCH, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 173,59, 173.21, 166.64, 161.77, 148.27, 147.23, 139.32, 135.21, 134,23, 129.16, 128.75, 128.34, 127,55, 127.12, 123.15, 64.75, 55.78; Anal. calcd. (%) for $C_{16}H_{16}N_4O_7$ (376.33): C, 51.07; H, 4.29; N, 14.89. Found (%): C, 51.13; H, 4.25; N, 14.92.

(*cis/trans*)1-(2,4-Dinitro-phenyl)-3-(4-methoxy-phenyl)-5-oxo-pyrazolidine-4-carboxylic acid (4d): m.p.: 229-230 °C; IR (KBr, ν_{max}, cm^{-1}): 3264.18, 3074.33, 2924.35, 1697.67, 1684.46, 1583.92, 1474.27; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.91 (m, 2xCHarom, 2H), 8.62 (br, s, 2xNH, 2xOH, 4H), 8.42-7.71 (m, Arom, 10H), 6,77-6.75 (m, 2xCHarom, 2H), 5.13-5.11 (m, 2xCH, 2H), 3.81 (s, 2xCH_3, 6H), 3.72-3.69 (m, 2xCH, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 175.01, 174.24, 166.65, 160.94, 159.19, 158.87, 147.13, 146.13, 139.12, 128.76, 128.24, 127.10, 126.23, 123.05, 114.15, 63.95, 56.28, 55.13; Anal. calcd. (%) for $C_{17}H_{18}N_4O_8$ (406.29): C, 50.25; H, 4.46; N, 13.79. Found (%): C, 51.20; H, 4.50; N. 13.78.

(*cis/trans*) 5-Oxo-1,3-diphenyl-pyrazolidine-4-carboxylic acid methyl ester (4e): m.p.: 130-131 °C; IR (KBr, ν_{max}, cm^{-1}): 3308.10, 3029.33, 1715.34, 1693.76, 1593,83, 1493,24; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7,92-7.81 (m, Ar, 10H), 7.39-7.23 (m, Ar, 10H), 5.12-5.08 (m, 2xCH, 2H), 4.70 (br, s, 2xNH, 2H), 3.78 (s, 2xCH_3, 6H), 3.61-3.58 (m, 2xCH, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.56, 168.22, 165.06, 138.92, 138.36, 136.67, 129.07, 128.84, 127.67, 127.10, 126.44, 124.36, 119.24, 64.48, 56.06, 51.56; Anal. calcd. (%) for $C_{17}H_{16}N_2O_3$ (296.33): C, 68.91; H, 5.44; N, 9.45. Found (%): C, 69.78; H, 5.42; N, 9.50.

(*cis/trans*) 3-(4-Methoxy-phenyl)-5-oxo-1-phenyl-pyrazolidine-4-carboxylic acid methyl ester (4f): m.p.: 105-106 °C; IR (KBr, ν_{max}, cm^{-1}): 3312.56, 3034.91, 1724.14, 1698.65, 1591.12, 1486.16; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.96-7.21 (m, Ar, 14H), 6.78-6.76 (m, Ar, 4H), 5.11-5.09 (m, 2xCH, 2H), 4.69 (br, s, 2xNH, 2H), 3.82 (s, 2xCH_3, 6H), 3.79 (s, 2xCH_3, 6H), 3.65-3.61 (m, 2xCH, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.83, 168.45, 168.44, 165.27, 158.12, 140.56, 130.46, 129.65, 129.39, 128.86, 127.82, 124.16, 119.35, 114.13, 63.75, 55.47, 55.46, 51.73; Anal. calcd. (%) for $C_{18}H_{18}N_2O_4$ (326.36): C, 66.25; H, 5.56; N, 8.58. Found (%): C, 66.26; H, 5.51; N, 8.60.

(*cis/trans*) 1-(2,4-Dinitro-phenyl)-5-oxo-3-phenyl-pyrazolidine-4-carboxylic acid methyl ester (4g): m.p.: 180-181 °C; IR (KBr, ν_{max}, cm^{-1}): 3322.15, 3079.27, 1702.73, 1693.24, 1587.13, 1496.32; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.97-8.96 (m, 2xCHarom, 2H), 8.50-7.32 (m, Ar, 14H), 5.9-5.7 (m, 2xCH, 2H), 4.80 (br, s, 2xNH, 2H), 3.78 (s, 2xCH_3, 6H), 3.55-3.52 (m, 2xCH, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 168.65, 168. 64, 166.43, 161.97, 146.63, 145.78, 140.09, 135.98, 134.43, 128.83, 127.74, 127.50, 126.33, 126.32, 121.63, 63.75, 55.29, 51.70; Anal. calcd. (%) for $C_{17}H_{18}N_4O_7$ (390.36): C, 52.31; H, 4.65; N, 14.35. Found (%): C, 52.33; H, 4.66; N, 14.30.

(*cis/trans*)1-(2,4-Dinitro-phenyl)-3-(4-methoxy-phenyl)-5-oxo-pyrazolidine-4-carboxylic acid methyl ester (4h): m.p.: 171-172 °C; IR (KBr, ν_{max}, cm^{-1}): 3309.98, 3025.83, 1708.78, 1693.88, 1598.09, 1490.06; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.97-8.96 (m, 2xCHarom, 2H), 8.52-7.74 (m, Ar, 10H), 6.73-6.70 (m, 2xCHarom, 2H), 5.10-5.7 (m, 2xCH, 2H), 4.81 (br, s, 2xNH, 2H), 3.82 (s, 2xCH_3, 6H), 3.80 (s, 2xCH_3, 6H), 3.54-3.50 (m, 2xCH, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 168.68, 166.47, 162.02, 157.63, 146.62, 145.82, 140.12, 129.72, 129.14, 128.60, 128.35, 127.86, 125.74, 121.51, 112.85, 63.76, 55.45, 55.44 51.72; Anal. calcd. (%) for $C_{18}H_{20}N_4O_8$ (420.38): C, 51.43; H, 4.80; N, 13.33. Found (%): C, 51.45; H, 4.77; N, 13.34.

5-Amino-1,3-diphenyl-2,3-dihydro-1*H*-pyrazole-4-carbonitrile (5a): m.p.: 98-99 °C; IR (KBr, ν_{max}, cm^{-1}): 3315.18, 3021.33, 2271.04, 1591.00, 1483.33; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.27 (br, s, NH_2, NH, 3H), 8.05-7.99 (m, Ar, 2H), 7.32-9.97 (m, Ar, 8H), 4.34 (s, CH, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 154. 35, 145.64, 137.06, 130.10, 129.36, 128.49, 128.08, 126.47, 124.79, 119.16, 112.37, 89.92, 54.67; Anal. calcd. (%) for $C_{16}H_{14}N_4$ (262.32): C, 73.26; H, 5.38; N, 21.36. Found (%): C, 73.23; H, 5.42; N, 21.32.

5-Amino-3-(4-methoxy-phenyl)-1-phenyl-2,3-dihydro-1*H*-pyrazole-4-carbonitrile (5b): m.p.: 102-103 °C; IR (KBr, ν_{max}, cm^{-1}): 3305.18, 3060.16, 2217.20, 1593.83, 1490.41; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.31 (br, s, NH_2, NH, 3H), 7.60-7.30 (m, Ar, 4H), 7,07-6.87 (m, Ar, 5H), 4.34 (s, CH, 1H), 3.86 (s, CH_3, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 159. 76, 153.87, 145.91, 129.59, 128.86, 127.52, 118.96, 115.62, 114.66, 112.25, 89.92, 56.03, 54.57; Anal. calcd. (%) for $C_{17}H_{16}N_4O$ (292.33): C, 69.85; H, 5.52; N, 19.16. Found (%): C, 69.83; H, 5.55; N, 19.15.

5-Amino-1-(2,4-dinitro-phenyl)-3-phenyl-2,3-dihydro-1*H*-pyrazole-4-carbonitrile (5c): m.p.: 160-161 °C; IR (KBr, ν_{max}, cm^{-1}): 3337.67, 3043.42, 2197.64, 1578.27, 1487.25; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.26 (br, s, NH_2, NH, 3H), 8.97-7.76 (m, Ar, 5H), 7,31-7.11 (m, Ar, 2H), 4.36 (s, CH, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 155.26, 145.60, 145.32, 141.83, 136.97, 130.64, 129.16, 127.69, 127.26, 126.57, 125.74, 122.66, 118.95, 112.37, 89.87, 54.48; Anal. calcd. (%) for $C_{16}H_{16}N_6O_4$ (356.34): C, 53.93; H, 4.53; N, 23.58. Found (%): C, 53.90; H, 3.57; N, 23.55.

5-Amino-1-(2,4-dinitro-phenyl)-3-(4-methoxy-phenyl)-2,3-dihydro-1*H*-pyrazole-4-carbonitrile (5d): m.p.: 154-155 °C; IR (KBr, ν_{max}, cm^{-1}): 3318.83, 3023.41, 2223.13, 1581.93, 1493.03; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.30 (br, s, NH_2, NH, 3H), 8.97-7.76 (m, Ar, 3H), 7.57-6.98 (m, Ar, 4H), 4.36 (s, CH, 1H), 3.84 (s, CH_3, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 158.98, 156.82, 145.61, 145.49, 142.15, 128.30, 128.27, 127.89, 125.70, 122.74, 118.93, 116.43, 89.86, 55.59, 54.58; Anal. calcd. (%) for $C_{17}H_{18}N_6O_5$ (386.37): C, 52.85; H, 4.70; N, 21.75. Found (%): C, 52.87; H, 4.72, N, 21.70.

RESULTS AND DISCUSSION

In continuing our research on the applications of ball milling in organic synthesis [65], we reported a green, effective and high-yield one-pot synthesis of novel 5-oxo-pyrazolidine and 5-amino-2,3-dihydro-1*H*-pyrazole derivatives. In this technique, three components, namely, aldehyde, phenyl hydrazine/3,4-dinitrophenyl hydrazine and malonic derivatives, are directly condensed through simple ball milling without adding any solvent or catalyst (**Scheme-I**).

To optimize the synthesis of 5-oxo-pyrazolidines and 5-amino-2,3-dihydro-1*H*-pyrazoles, we placed equimolar quantities (0.02 mol) of benzaldehyde, phenylhydrazine and malonic acid (with a total mass of 6.36 g) in a stainless steel bowl; we subsequently added 31.80 g of balls (ratio of ball weight to reagent weight is equal to 5) [66]. The progress of the reaction was monitored every 10 min milling cycle using thin-layer chromatography (TLC). The reaction was completed after 60 min. Similar conditions were applied to different reactions and reaction times are presented in Table-1.

TABLE-1
MILLING TIME AND YIELDS OF 5-OXO-PYRAZOLIDINE AND 5-AMINO-2,3-DIHYDRO-1*H*-PYRAZOLE DERIVATIVES USING RATIO (BALLS WEIGHT/REAGENTS WEIGHT) EQUAL TO 5

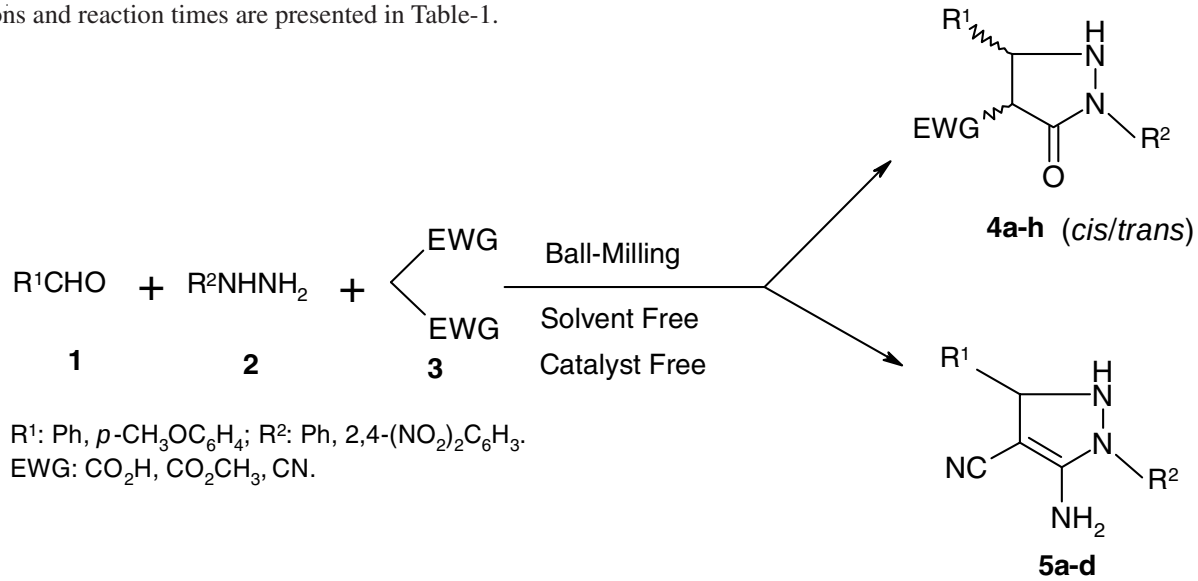
Compound	Milling time (min)	Compound	Milling time (min)
4a	60	**4g**	50
4b	60	**4h**	50
4c	60	**5a**	40
4d	60	**5b**	40
4e	50	**5c**	40
4f	50	**5d**	40

The structures of the synthesized products were established through their spectroscopic data. All products **4a-h** (5-oxo-pyrazolidines) were obtained in a mixture of *cis* and *trans* diastereomers (**Scheme-I**). The diastereoisomers of **4a-h** were difficult to separate by silica gel column chromatography and various attempts to achieve the separation of the diastereoisomers using an appropriate chromatographic column size were undertaken. These methods have not been successful and the diastereomeric ratio of **4a-h** (Table-2) was only raised by ^{1}H NMR analysis.

An interesting signals is detected in the ^{1}H NMR spectra for **4a-h** (5-oxo-pyrazolidines). These signals are located at approximately 5.07-5.18 and 3.50-3.73 ppm belong to the two CH in the diastereomeric pyrazolidine rings. The products **5a-d** (5-amino-2,3-dihydro-1*H*-pyrazoles) show a characteristic single peak in the ^{1}H NMR spectra at approximately 4.34-4.36 ppm; this peak corresponds to the allylic proton in the pyrazole ring. The signal in the ^{13}C NMR spectra at approximately 89.86-89.92 ppm belong to the α-C of the nitrile group.

Conclusion

In conclusion, we reported a green, simple and operational synthesis of new different 5-oxo-pyrazolidine and 5-amino-2,3-dihydro-1*H*-pyrazole derivatives (Table-2) using ball milling method. This economical and eco-friendly process can synthesize all products in pure form without further purification and obtain high yields.



Scheme-I: Synthesis of diastereomeric 5-oxo-pyrazolidines and 5-amino-2,3-dihydro-1*H*-pyrazoles

TABLE-2
SYNTHESIZED OF DIASTEREOMERIC 5-OXO-PYRAZOLIDINES AND 5-AMINO-2,3-DIHYDRO-1*H*-PYRAZOLES USING BALL MILL

Entry	R^1	R^2	EWG	Product	Yield (%)	dr[a]
1	Ph	Ph	CO_2H	**4a**	95	31:69
2	*p*-OCH_3-C_6H_4	Ph	CO_2H	**4b**	95	30:70
3	Ph	2,4-dinitro-C_6H_3	CO_2H	**4c**	91	28:72
4	*p*-OCH_3-C_6H_4	2,4-dinitro-C_6H_3	CO_2H	**4d**	90	29:71
5	Ph	Ph	CO_2CH_3	**4e**	96	27:73
6	*p*-OCH_3-C_6H_4	Ph	CO_2CH_3	**4f**	97	32:68
7	Ph	2,4-dinitro-C_6H_3	CO_2CH_3	**4g**	92	25:75
8	*p*-OCH_3-C_6H_4	2,4-dinitro-C_6H_3	CO_2CH_3	**4h**	91	24:76
9	Ph	Ph	CN	**5a**	98	–
10	*p*-OCH_3-C_6H_4	Ph	CN	**5b**	97	–
11	Ph	2,4-dinitro-C_6H_3	CN	**5c**	93	–
12	*p*-OCH_3-C_6H_4	2,4-dinitro-C_6H_3	CN	**5d**	92	–

[a]Diastereomeric ratio (*cis*/*trans*) was calculated by ^{1}H NMR analysis of the mixtures of **4a-h**.

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