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$Mg(HSO_4)_2$: an efficient and eco-friendly catalyst for the synthesis of pyrazoles

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$Mg(HSO_4)_2$ is an efficient, readily available, and eco-friendly catalyst for the synthesis of 1,3,5-trisubstituted or 1,3,4,5-tetrasubstituted pyrazoles via the condensation of 1,3-diketones and hydrazine. Mild condition, simplicity of procedure, high yields, easy work-up and short reaction time are some advantages of this green protocol.

Key words: $Mg(HSO_4)_2$, 1, 3-diketones, hydrazine, pyrazole, 1,3,5-substituted pyrazoles, 1,3,4,5-tetrasubstituted pyrazoles

INTRODUCTION

Pyrazole derivatives have a wide range of biological activities. They can be used as anti-inflammatory [1, 2], antipyretic [3], gastric secretion stimulatory [4], antidepressant [5], antirheumatoid arthritis [6, 7], antibacterial [8], anticonvulsant [9], antitumor [10], antipsychotic [11], antimicrobial [12], antiviral [13], antifungal, and antifilarial agents [14]. They also serve as herbicides [15], fungicides [16], pesticides [17], dyestuffs [18] and insecticides [19].

Pyrazoles can be synthesized via 1,3-dipolar cycloaddition of diazo compounds [20], reaction of chalcones and hydrazines [21], a four-component coupling of terminal alkynes, hydrazine, carbon monoxide, and aryl iodides [22], and the direct condensation of 1,3-diketones and hydrazines in the presence of an acidic catalyst [23]. The last one is the simplest and the most straightforward procedure for the synthesis of pyrazoles. A variety of catalysts such as H_2SO_4 [24], polystyrene supported sulfonic acid [25], layered zirconium sulfophenyl phosphonate [a-$Zr(CH_3PO_3)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}$] [26], $Sc(OTf)_3$ [27], and Y-zeolite [28] have been employed to affect this transformation.

$Mg(HSO_4)_2$ [29] has many advantages such as low cost, ease of preparation, high efficiency, eco-friendly and easy work-up. $Mg(HSO_4)_2$ was used as a catalyst for oxidation of thiols [30], sulfides [31], for synthesis of dihydropyridines [32], urazoles and bis-urazoles [33], acetate and formate esters [34, 35], preparation of α-alkoxy alcohols from epoxides [36], hydrolysis of acetals and ketals [37], oximes, hydrazones and semicarbazones [29], mono nitration of phenol [38], aldol condensation [39], and stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenyl phosphoranylidene) butanedioates to electron-poor (*Z*)-*N*- vinylimides under solvent-free conditions [40].

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RESULTS AND DISCUSSION

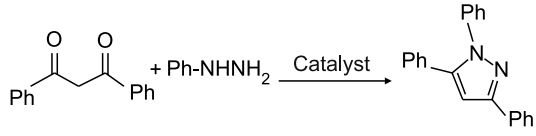
In continuation of our investigations on the applications of solid acids in organic synthesis, we have studied the synthesis of pyrazole derivatives in the presence of $Mg(HSO_4)_2$ via condensation of 1,3-diketones and hydrazines. The reaction of phenylhydrazine (1 mmol) with 1,3-diphenyl-1,3-propanedione (1 mmol) was investigated for the optimization of the reaction conditions (Table 1). At different temperatures and various molar ratios of substrates in the presence of $Mg(HSO_4)_2$,the reaction revealed that the best conditions were solvent-free at 60 °C and a molar ratio of 1,3-diketone: hydrazine derivatives: $Mg(HSO_4)_2$ of 1 : 1 : 0.10 g.

Herein, we report that $Mg(HSO_4)_2$ is an efficient and reusable catalyst for the synthesis of pyrazole derivatives and is comparable with some other applied catalysts (Table 1). To study the reusability of $Mg(HSO_4)_2$, after each run, the product was dissolved to $CHCl_3$ and filtered. The catalyst residue was washed with diethyl ether and reused. Treatment with $CHCl_3$ removes the tar from the catalyst surface more efficiently (Table 1, entries 12 and 13). The catalyst was reusable although a gradual decline was observed in its activity.

The applicability of the present method to a large scale process was examined with 20 mmol of 2,4-dinitrophenylhydrazine and 20 mmol of 1,3-diphenyl-1,3-propanedione under thermal conditions which gave 1-(2,4-dinitrophenyl)-3,5-diphenyl-pyrazole in a 90% yield. 1,3-Diketones and various hydrazines were used as substrates for the synthesis of pyrazoles in the presence of $Mg(HSO_4)_2$ at 60 °C under solvent-free condition (Scheme and Table 2).

In conclusion, we have demonstrated a simple method for the synthesis of pyrazoles using $Mg(HSO_4)_2$ as an eco-friendly, readily available, inexpensive and efficient catalyst. Clean process, short reaction time, scale-up, high yields, simple procedure, easy work-up, and green conditions are the advantages of this protocol.

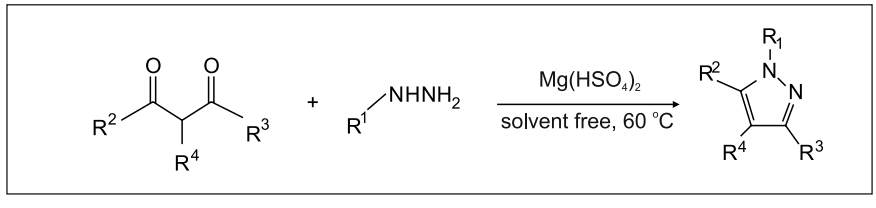
Table 1. **Synthesis of 1,3,5-triphenyl-pyrazole in various conditions**[a]



Entry	Catalyst/g	Solvent	Conditions	Time, min	Yield, %	Ref.
1	$Mg(HSO_4)_2$/0.06	Chloroform	r. t.	20	55	–
2	$Mg(HSO_4)_2$/0.08	Chloroform	r. t.	15	68	–
3	$Mg(HSO_4)_2$/0.10	Chloroform	r. t.	15	72	–
4	$Mg(HSO_4)_2$/0.10	Chloroform	Reflux	15	82	–
5	$Mg(HSO_4)_2$/0.06	Ethanol	r. t.	20	45	–
6	$Mg(HSO_4)_2$/0.08	Ethanol	r. t.	15	57	–
7	$Mg(HSO_4)_2$/0.10	Ethanol	r. t.	15	63	–
8	$Mg(HSO_4)_2$/0.10	Ethanol	Reflux	15	75	–
9	$Mg(HSO_4)_2$/0.06	Solvent-free	r. t.	20	52	–
10	$Mg(HSO_4)_2$/0.08	Solvent-free	r. t.	15	64	–
11	$Mg(HSO_4)_2$/0.10	Solvent-free	60 °C	15	98	–
12	$Mg(HSO_4)_2$/0.10 (2nd run)	Solvent-free	60 °C	15	93	–
13	$Mg(HSO_4)_2$/0.10 (3rd run)	Solvent-free	60 °C	15	91	–
14[b]	H_2SO_4 (0.1 drop)	Solvent-free	r. t.	1	86	24
15[b]	Polystyrene supported sulfonic acid (0.1 mL of 20% PSSA solution)	Solvent-free	r. t.	0.04	92	25
16[b]	$[a\text{-}Zr(CH_3PO_3)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}]$ (0.025)	Solvent-free	40 °C	2	95	26
17[b]	$Sc(OTf)_3$ (2 mol%)	Solvent-free	r. t.	0.35	94	27
18[b]	Y-Zeolite (1)	Ethylene dichloride	r. t.	2	84	28

[a] Phenylhydrazine (1 mmol) and 1,3-diphenyl-1,3-propanedione (1 mmol) were applied.

[b] Phenylhydrazine (1 mmol) and 2,4-pentanedione (1 mmol) were applied.



Scheme

Table 2. **Condensation of 1,3-diketones (1 mmol) and hydrazine (1 mmol) in the presence of $Mg(HSO_4)_2$ (0.10 g) at 60 °C**

Entry	R^1	R^3	R^4	R^2	Yield[b], %	Mp, °C	Ref.
1	C_6H_5	C_6H_5	H	C_6H_5	90	137–138	28
2	C_6H_5	C_6H_5	H	CH_3	87	55–57	27
3	C_6H_5	CH_3	H	CH_3	87	Oil	27
4	C_6H_5	CH_3	Cl	CH_3	91	Oil	25
5	2,4-$(O_2N)_2$-C_6H_3	C_6H_5	H	C_6H_5	93	149–150	–
6	2,4-$(O_2N)_2$-C_6H_3	C_6H_5	H	CH_3	90	128–130	26
7	2,4-$(O_2N)_2$-C_6H_3	CH_3	H	CH_3	85	121–122	27
8	2,4-$(O_2N)_2$-C_6H_3	CH_3	Cl	CH_3	88	167–168	–
9	H	C_6H_5	H	C_6H_5	79	200–201	–
10	H	CH_3	H	CH_3	97	107–109	24
11	H	C_6H_5	H	CH_3	79	203–205	24
12	2-Cl-C_6H_4	C_6H_5	H	C_6H_5	91	126–127	–
13	4-Br-C_6H_4	CH_3	Cl	CH_3	86	87–88	–
14	4-Br-C_6H_4	C_6H_5	H	C_6H_5	90	117–119	–
15	4-Me-C_6H_4	C_6H_5	H	C_6H_5	89	104–105	–
16	4-Me-C_6H_4	CH_3	H	CH_3	88	Oil	24
17	4-OMe-C_6H_4	C_6H_5	H	C_6H_5	78	Oil	–
18	4-OMe-C_6H_4	C_6H_5	H	CH_3	82	Oil	–
19	4-Me-$C_6H_4SO_2$	CH_3	H	CH_3	87	94–95	27
20	4-Me-$C_6H_4SO_2$	C_6H_6	H	C_6H_6	85	101–103	–
21	4-Me-$C_6H_4SO_2$	C_6H_6	H	CH_3	89	86–87	–

EXPERIMENTAL

General

The products were characterized by an elemental analysis, IR, ^{1}H-NMR, and ^{13}C-NMR spectra. IR spectra were run on a Bruker, Eqinox 55 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were obtained using Bruker Avance 400 and 500 MHz spectrometers (DRX). The elemental analysis was done by a Costech ECS 4010 CHNS-O analyser. Melting points were determined by a Buchi melting point B-540 B. V. CHI apparatus. A Shimadzu QP-1100 EX mass spectrometer was employed for recording all mass spectra. The ion source was operated at 70 eV under a pressure of 5×10^{-6} Torr and a temperature of 250 °C.

General procedure for the synthesis of pyrazole derivatives

A mixture of 1,3-diketone (1 mmol), hydrazine derivatives (1 mmol) and $Mg(HSO_4)_2$ (0.10 g) was stirred at 60 °C. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was washed with chloroform and filtered to recover the catalyst. The filtrate was evaporated and the crude product was recrystallized from *iso*-propanol to afford the pure pyrazole derivatives in 78–93% yields.

1,3,5-Triphenyl-pyrazole **(Table 2, entry 1)**

FT-IR (ATR, neat) 1 594, 1 495, 1 455, 1 362, 971, 920, 814, 764, 693 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 6.84 (s, 1H), 7.40 (m, 13H), 7.97 (d, J = 8.4 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 105.64, 125.74, 126.26, 127.85, 128.43, 128.73, 128.91, 129.08, 129.19, 129.34, 131.04, 133.50, 140.60, 144.83, 152.41.

1,3-Diphenyl-5-methyl-pyrazole **(Table 2, entry 2)**

FT-IR (ATR, neat): 1 596, 1 457, 763, 695 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 2.40 (s, 3H), 6.33 (s, 1H), 7.23–7.41 (m, 10H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.0, 14.0, 104.8, 108.2, 125.1, 125.4, 125.6, 126.2, 127.4, 127.5, 128.0, 128.2, 128.5, 128.8, 129.0, 129.1, 129.3, 129.5, 130.1, 131.2, 140.6, 144.1, 149.8.

1-Phenyl-3,5-dimethyl-4-chloropyrazole **(Table 2, entry 4)**

FT-IR (ATR, neat): 1 597, 1 504, 760, 696 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.31 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 7.38–7.42 (m, 3H), 7.45–7.49 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.2, 11.8, 110.2, 124.9, 128.1, 129.6, 129.6, 136.1, 140.2, 146.5.

1-(2,4-Dinitrophenyl)-3,5-diphenyl-pyrazole **(Table 2, entry 5)**

FT-IR (ATR, neat): 1 607, 1 536, 1 491, 1 459, 1 344, 1 076, 832, 762, 691 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 6.92 (s, 1H), 7.4 (m, 9H), 7.86 (d, J = 10.4 Hz, 2H), 8.37 (dd, J = 10.4 and 3.5 Hz, 1H), 8.74 (d, J = 3.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): 107, 121, 126.4, 127.4, 129, 129.2, 129.3, 129.5, 129.9, 130, 132.2, 138.5, 146.3, 146.4, 155, M. S. (E.I, m/z) = 386, 293, 190, 105 and 77. Anal. calcd. for $C_{21}H_{14}N_4O_4$: C, 65.28; H, 3.65; N, 14.50, Found: C, 64.1; H, 3.2; N, 14.4.

1-(2,4-Dinitrophenyl)-3-phenyl-5-methyl-pyrazole **(Table 2, entry 6)**

FT-IR (ATR, neat): 1 609, 1 538, 1 505, 766, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 2.38 (s, 3H), 6.41 (s, 1H), 7.22 (d, J = 6.4, 2H), 7.27–7.39 (m, 3H), 7.44 (d, J = 8.8, 1H), 8.32 (dd,

J = 14.4, 2.4, 1H), 8.70 (d, *J* = 2.4, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.0, 109.8, 121.3, 127.5, 128.9, 129.1, 129.2, 129.5, 129.6, 130.1, 138.7, 145.7, 146.2, 153.1.

1-(2,4-Dinitrophenyl)-3,5-dimethyl-pyrazole **(Table 2, entry 7)**
FT-IR (ATR, neat): 1 607, 1 529, 1 480, 1 344, 1 104, 1 029, 903, 848, 834, 795 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 2.3 (s, 6H), 7.70 (d, 1H), 8.57 (dd, 1H), 8.85 (d, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.6, 11.8, 112.7, 121.6, 127.9, 129.7, 137.5, 137.9, 149.9. Anal. calcd. for $C_{11}H_9ClN_4O_4$: C, 44.53; H, 3.06; Cl, 11.92; N, 18.89; O, 21.57. Found: C, 46.6; H, 3.0; N, 18.7; O and Cl, 31.7.

1-(2,4-Dinitrophenyl)-3,5-dimethyl-4-chloropyrazole **(Table 2, entry 8)**
FT-IR (ATR, neat): 1 614, 1 531, 1 425, 1 342, 1 133, 1 105, 1 029, 904, 833, 743 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 2.3 (s, 6H), 7.70 (d, *J* = 10.5 Hz, 1H), 8.57 (dd, *J* = 10.5 and 3.4 Hz, 1H), 8.83 (d, *J* = 3.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.6, 11.8, 112.7, 121.6, 127.9, 129.7, 137.5, 137.9, 149.9, M. S. (E.I, m/z) = 298, 297, 296, 129, 101 and 75. Anal. calcd. for $C_{11}H_9ClN_4O_4$: C, 44.53; H, 3.06; Cl, 11.92; N, 18.89. Found: C, 46.6; H, 3.0; N, 18.7.

3,5-Diphenyl-1H-pyrazole **(Table 2, entry 9)**
FT-IR (ATR, neat) 1 605, 1 461, 1 316, 1 181, 1 075, 1 000, 753, 687 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 6.99 (s, 1H), 7.41 (m, 6H), 7.8 (d, 4H, *J* = 8.5 H_Z); ^{13}C-NMR (100 MHz, $CDCl_3$): 100.1, 125.7, 128.2, 128.8, 131.3, 148.8. Anal. calcd. for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.8; H, 5.7; N, 12.5.

3-Phenyl-5-methyl-1H-pyrazole **(Table 2, entry 11)**
FT-IR (ATR, neat): 2 400–3 400, 1 613, 1 595, 1 465, 777, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 2.61 (s, 3H), 6.558 (s.1H), 7.514 (d, *J* = 7.6, 3H), 7.957 (d, *J* = 6.4, 2H), 9.5–10.5 (sbr, NH). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.2, 103.4, 126.0, 127.0, 129.4, 130.9, 145.5, 146.9. Anal. calcd. for $C_{10}H_{10}N_2$: C, 45.3; H, 3.06; Cl, 11.92; N, 18.89; O, 21.57. Found: C, 46.6; H, 3.0; N, 18.7.

1-(2-Chlorophenyl)-3,5-diphenyl-pyrazole **(Table 2, entry 12)**
FT-IR (ATR, neat): 1 598, 1 543, 1 488, 1 458, 1 360, 1 212, 1 074, 971, 806, 757, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 6.90 (s, 1H), 7.45 (m, 12H), 7.94 (d, *J* = 8.4 Hz, 2H), M. S. (E.I, m/z) = 332, 331, 330, 295, 192, 111, 91 and 77.

1-(4-Bromophenyl)-3,5-dimethyl-4-chloropyrazole **(Table 2, entry 13)**
FT-IR (ATR, neat): 1 588, 1 501, 1 470, 1 401, 1 380, 1 366, 1 100, 1 071, 1 037, 1 008, 831, 810, 795 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 2.32 (s, 3H), 2.33 (s, 3H), 7.31 (d, *J* = 8.6 Hz 2H), 7.6 (d, *J* = 8.6 Hz, 2H,), M. S. (E.I, m/z) = 288, 286, 284, 169, 155, 102, 77 and 75. Anal. calcd. for $C_{11}H_{10}BrClN_2$: C, 46.26; H, 3.53; N, 9.81. Found: C, 48.9; H, 3.3; N, 10.0.

1-(4-Bromophenyl)-3,5-diphenyl-pyrazole **(Table 2, entry 14)**
FT-IR (ATR, neat): 1 588, 1 546, 1 491, 1 457, 1 399, 1 362, 1 209, 1 063, 1 010, 969, 831, 809, 764, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 6.83 (s, 1H), 7.36 (m, 12H), 7.92 (d, 2H).

1-(4-Methylphenyl)-3,5-diphenyl-pyrazole **(Table 2, entry 15)**
FT-IR (ATR, neat): 1 598, 1 511, 1 462, 1 361, 972, 822, 760, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 2.38 (s, 3H), 6.83 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.30 (m, 6H), 7.44 (t, *J* = 8.4 Hz, 2H,) 7.93 (d, *J* = 8.4 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21, 104, 125.2, 125.8, 128, 128.3, 128.5, 128.7, 128.8, 129.5, 130.6, 133, 137.5, 137.6, 144.4, 151.7, M. S. (E.I, m/z) = 310, 91 and 77. Anal. calcd. for $C_{22}H_{18}N_2$: C, 85.2; H, 5.58; N, 9.03. Found: C, 85.2; H, 5.8; N, 8.7.

1-(4-Methoxyphenyl)-3-phenyl-5-methyl pyrazole **(Table 2, entry 18)**
FT-IR (ATR, neat): 1 607, 1 571, 1 514, 1 250, 1 030, 834, 747, 696, 666, 624. ^{1}H NMR (400 MHz, $CDCl_3$): 2.5 (s, 3H), 3.8 (s, 3H), 6.4 (s, 1H), 6.88 (d, 2H, *J* = 8 Hz), 7.3 (d, 4H, J = 6.4 Hz), 7.3 (m, 3H).

1-(4-Tolosulfono)-3,5-dimethyl pyrazole **(Table 2, entry 19)**
FT-IR (ATR, neat): 1 598, 1 574, 1 370, 1 292, 1 192, 1 175, 1 126, 968, 813, 757, 703, 669 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 2.2 (s, 3H), 2.4 (s, 3H), 2.5 (s, 3H), 5.9 (s, 1H), 7.3 (d, 2H, *J* = 8.2 Hz), 7.8 (d, 2H, *J* = 8.2 Hz).

1-(4-Tolosulfono)-3,5-diphenyl pyrazole **(Table 2, entry 20)**
FT-IR (ATR, neat): 1 594, 1 558, 1 485, 1 459, 1 380, 1 192, 1 175, 1 102, 942, 759, 684, 658 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 2.1 (s, 3H), 6.81 (s, 1H), 6.93 (d, 2H, *J* = 7.8 Hz), 7.22 (m, 6H), 7.53 (d, 2H, *J* = 7.8 Hz), 7.62 (m, 4H), M. S. (E.I, m/z) = 375, 311, 191, 91 and 77.

1-(4-Tolosulfono)-3(5)-phenyl-5(3)-methyl pyrazole **(Table 2, entry 21)**
FT-IR (ATR, neat): 1 594, 1 564, 1 460, 1 375, 1 294, 1 190, 1 123, 1 076, 811, 768, 689, 670 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 2.4 (s, 3H), 2.6 (s, 3H), 6.4 (s, 1H), 7.32 (d, 2H, *J* = 8.2 Hz), 7.4 (m, 3H), 7.8 (d, 2H, *J* = 6.8 Hz), 7.9 (d, 2H, *J* = 8.2 Hz), M. S. (E.I, m/z) = 312, 248, 128 and 91.

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MG(HSO$_4$)$_2$ – EFEKTYVUS IR EKOLOGIŠKAS KATALIZATORIUS PIRAZOLŲ SINTEZEI

S a n t r a u k a

Parodyta, kad Mg(HSO$_4$)$_2$ yra efektyvus, lengvai prieinamas ir ekologiškas katalizatorius 1,3,5-tripavaduotų ir 1,3,4,5-tetrapavaduotų pirazolų sintezei, atliekamai kondensuojant 1,3-diketonus su hidrazinu.