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$Mg(ClO_4)_2$: AN EFFICIENT CATALYST FOR THE SYNTHESIS OF 1,3,5-TRISUBSTITUTED PYRAZOLES

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An efficient, convenient and solvent-free procedure for synthesis of pyrazoles via condensation of 1,3- diketones and hydrazines in the presence of magnesium perchlorate is described. This protocol has the advantages of high yields, easy workup, short reaction times, and green conditions**.**

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Keywords: Trisubstituted Pyrazoles**,** *$Mg(ClO_4)_2$*, Hydrazines, 1, 3- diketones

1. Introduction

Pyrazole based compounds have a wide variety of biologically activities. These important materials can be used as anti-inflammatory [1], antipyretic [2], gastric secretion stimulatory [3], antidepressant [4], anti rheumatoid arthritis [5], antibacterial [6], anticonvulsant [7] antitumor [8], antipsychotic [9], antimicrobial [10], antiviral [11], antifungal and antifilarial agents [12]. Also serve as herbicides [13], fungicides [14], pesticides [15], dyestuffs [16], and insecticides [17].

Pyrazoles can be synthesized *via* 1,3-dipolar cycloadditions of diazo compounds [18], reaction of chalcones [19] and hydrazines, a four-component coupling of terminal alkynes, hydrazine, carbon monoxide, and aryl iodides [20], and the direct condensation of 1,3-diketones and hydrazines in the presence of an acidic catalyst [21]. The last one is the simplest and most straightforward procedure for the synthesis of pyrazoles. A variety of catalysts such as H_2SO_4 [22], polystyrene supported sulfonic acid [23], layered zirconium sulfophenyl phosphonate [a-$Zr(CH_3PO_3)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}$] [24], $Sc(OTf)_3$ [25], and Y-zeolite [26] have been employed to affect this transformation.

Magnesium perchlorat $Mg(ClO_4)_2$) as a white crystal, is moisture stable, non-toxic, cheap and commercially available material. Previously, it has gained much interest in the synthesis of 1,5- benzodiazepines [27], the diels-Alder reaction [28], the asymmetric reduction of carbonyl compounds [29], the knovenagel condensation [30], the synthesis of imines and phenyl hydrazines [31], the synthesis of t-butyl ethers [32], and the kabachnik- fields reaction [33].

2. Experimental section

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General: Products were characterized by 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 a Bruker Avans 400 and 500 MHz spectrometers (DRX). The elemental analysis was done by Costech ECS 4010 CHNS-O analyser. Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus.

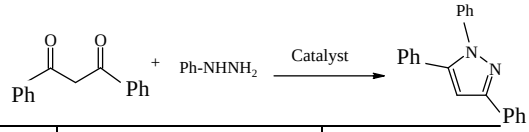
General procedure for the synthesis of pyrazole derivatives: 1,3-diketone (1 mmol), substituted hydrazine (1 mmol) and $Mg(ClO_4)_2$ (0.02 g) were placed in a round bottom flask and was heated at 70˚C. The Progress of the reaction was followed by TLC. After the completion of reaction, the crude mixture was solidified from mixture of ethanol and water. The pure product was obtained by recrystalization in ethanol.

3. Results and discussion

In continuation of our investigations on the applications of solid acids in organic synthesis [34], we investigated the synthesis of pyrazoles *via* the condensation of different 1,3-diketones and hydrazines in the presence of $Mg(ClO_4)_2$ as catalyst. The reaction of phenylhydrazine (1 mmol) with 1,3-diphenyl-1,3-propanedione (1 mmol) was investigated for optimization of the reaction conditions (Table 1). We have found that $Mg(ClO_4)_2$ is an efficient and reusable catalyst for the synthesis of pyrazole derivatives and it is comparable with some other catalysts. The reaction was done at different temperatures and various molar ratio of substrates in the presence of $Mg(ClO_4)_2$. The best condition was solvent-free at 70 ºC and a molar ratio of 1,3-diketone, hydrazine derivatives and $Mg(ClO_4)_2$ equal to : 1 : 1 : 0.02 g (8 mol%). The reusability of the $Mg(ClO_4)_2$ catalyst was also examined. After each run, the product was dissolved in $CHCl_3$ 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, entry21). The catalyst was reused although a gradual decline was observed in its activity. The applicability of the present method to a large scale process was examined with 15 mmol of 2,4-dinitrophenylhydrazine and 15 mmol of 3-chloro-2,4-pentanedione under thermal conditions which gave 1-(2,4-dinitrophenyl)-3,5-diphenyl-pyrazole in 94% yield. We believe that the current method is simple, efficient and less time-consuming for the synthesis of pyrazoles.

1,3-diketones and various hydrazines were used as substrates for the synthesis of pyrazoles under solvent-free condition at 70 °C (Scheme 1 and Table 2).

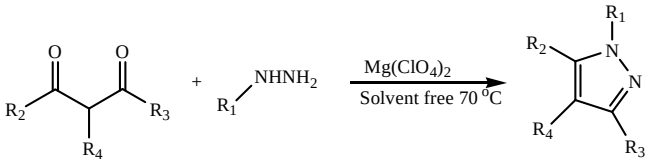
Table 1.Synthesis of 1,2,3-triphenyl -pyrazole in various conditions.[a]



Entry	Catalyst (g, mol %))	Solvent	Conditions	Time (h)	Yield (%)	Ref.
1	-	Solvent-free	r.t.	2	20	-
2	-	Solvent-free	70 °C	2	25	-
3	$Mg(ClO_4)_2$ (0.01, 4)	Solvent-free	r.t.	1.5	35	-
4	$Mg(ClO_4)_2$ (0.01, 4)	Solvent-free	70 °C	1.5	67	-
5	$Mg(ClO_4)_2$ (0.02, 8)	Solvent-free	r.t.	1	63	
6	$Mg(ClO_4)_2$ (0.02, 8)	Solvent-free	70 °C	1	90	-
7	$Mg(ClO_4)_2$ (0.03, 12)	Solvent-free	r.t.	1	67	-
8	$Mg(ClO_4)_2$ (0.03, 12)	Solvent-free	70 °C	1	92	-
9	$Mg(ClO_4)_2$ (0.02, 8)	Water	r.t.	10	25	-
10	$Mg(ClO_4)_2$ (0.02, 8)	Water	70 °C	10	40	-
11	$Mg(ClO_4)_2$ (0.02, 8)	Ethanol	r.t.	1.5	60	-
12	$Mg(ClO_4)_2$ (0.02, 8)	Ethanol	70 °C	1.5	85	-

13	$Mg(ClO_4)_2$ (0.02, 8)	Chloroform	r.t.	8	40	-
14	$Mg(ClO_4)_2$ (0.02, 8)	Chloroform	70 °C	8	65	-
15	$Mg(ClO_4)_2$ (0.02, 8)	*n*-Hexane	r.t.	10	15	-
16	$Mg(ClO_4)_2$ (0.02, 8)	*n*-Hexane	70 °C	10	35	-
17	$Mg(ClO_4)_2$ (0.02, 8)	Ethyl acetate	r.t.	5	45	
18	$Mg(ClO_4)_2$ (0.02, 8)	Ethyl acetate	70 °C	5	80	-
19	$Mg(ClO_4)_2$ (0.02, 8)	Dichloromethane	r.t.	3	33	-
20	$Mg(ClO_4)_2$ (0.02, 8)	Dichloromethane	70 °C	3	55	-
21[b]	$Mg(ClO_4)_2$ (0.02, 8)2th run	Solvent-free	70 °C	0.36	84	-
22[c]	H_2SO_4 (0.1 drop)	Solvent-free	r.t.	1	86	22
23[c]	polystyrene supported sulfonic acid(0.1 mL of 20% PSSA solution)	Solvent-free	r.t.	0.04	92	23
24[c]	[a-$Zr(CH_3PO_3)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}$](0.025)	Solvent-free	40 °C	2	95	24
25[c]	$Sc(OTf)_3$ (2 mol%)	Solvent-free	r.t.	0.35	94	25
26[c]	Y-Zeolite (1)	Ethylene dichloride	r.t.	2	84	26

[a] phenylhydrazine (1mmol) and 1,3-diphenyl-1,3-propanedione (1 mmol) were applied.
[b] 2,4-dinitrophenylhydrazine (1mmol) and 3-chloro-2,4-pentanedione (1 mmol) were applied.
[c] phenylhydrazine (1mmol) and 2,4-pentanedione (1 mmol) were applied.



Scheme 1

Table 2. Condensation of 1,3-diketones (1 mmol) and hydrazine s(1 mmol) in the presence of $Mg(ClO_4)_2$ (0.02g) at 70 °C.

Entry	R_1	R_2	R_4	R_3	Yield[b] (%)	Time (min)	Mp (°C)	Ref.
1	2,4- O_2N-C_6H_4	C_6H_5	H	C_6H_5	95	25	149-150	-
2	2,4- O_2N-C_6H_4	C_6H_5	H	CH_3	93	20	128-130	24
3	2,4- O_2N-C_6H_4	CH_3	H	CH_3	96	15	122-123	25
4	2,4- O_2N-C_6H_4	CH_3	Cl	CH_3	92	22	167-168	-
5	C_6H_4	C_6H_5	H	C_6H_5	90	60	137-138	26
6	C_6H_4	C_6H_5	H	CH_3	87	35	55-57	25
7	C_6H_4	CH_3	H	CH_3	89	25	oil	25
8	C_6H_4	CH_3	Cl	CH_3	80	15	oil	23
9	H	C_6H_5	H	CH_3	74	25	203-205	22
10	4- Br-C_6H_4	CH_3	Cl	CH_3	88	35	87-88	-
11	4- Br-C_6H_4	C_6H_5	H	C_6H_5	85	30	117-119	-
12	4- Br-C_6H_4	C_6H_5	H	Me	87	27	178-180	-
13	4- Me-C_6H_4	C_6H_5	H	C_6H_5	89	20	104-105	-
14	4- Me-C_6H_4	C_6H_5	H	CH_3	78	13	82-84	-
15	4-OMe-	C_6H_5	H	C_6H_5	78	15	oil	-
16	C_6H_4	C_6H_5	H	CH_3	82	22	oil	-
17	4-OMe-	CH_3	H	CH_3	87	25	94-95	25
18	C_6H_4	C_6H_6	H	C_6H_6	85	40	101-103	-
19	4- Me-	C_6H_6	H	CH_3	89	32	86-87	-
	$C_6H_4SO_2$							
	4- Me-							
	$C_6H_4SO_2$							
	4- Me-							
	$C_6H_4SO_2$							

In summary, we have developed an improved, and environmentally friendly procedure for the solventless synthesis of pyrazoles in the presence of $Mg(ClO_4)_2$. This methodology offers several advantages such as excellent yields, short reaction times, mild reaction conditions and use of cheap, commercially available and non-corrosive catalyst.

Selected spectra data: 1-(2,4-dinitrophenyl)-3,5-diphenyl-pyrazole (table 2, entry1). IR (ATR, neat): 1607, 1536, 1491, 1459, 1344, 1076, 832, 762, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 6.92 (s, 1 H), 7.3 (d, 2H, J = 6 Hz), 7.4(d, 4H, J = 6.8 Hz), 7.44(d, 2H, J = 7.6), 7.5(d, 1 H, J = 8.8 Hz), 7.85(d, 2H, J = 7.2), 8.38(d,1H, J = 6.8 Hz), 8.75(s,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. Anal. calcd. for $C_{21}H_{14}N_4O_4$: C, 65.28; H, 3.65; N, 14.50; O, 16.56. Found: C, 64.1; H, 3.2; N, 14.4; O, 18.2.

1-(2,4-dinitrophenyl)-3,5-dimethyl-4-chloropyrazole(table 2, entry 4). IR (ATR, neat): 1607, 1529, 1480, 1344, 1104, 1029, 903, 848, 834, 795 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 2.3 (s, 6 H), 7.70(d, 1H), 8.57 (dd, 1 H), 8.85 (d, 1 H) ^{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.

1,3,5-triphenyl-pyrazole (table 2, entry 5).IR (ATR, neat): 1596, 1495, 1483, 1456, 1363, 971, 920, 763, 691 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 6.85 (s, 1 H), 7.35 (m, 10H), 7.5 (t, 3 H, J = 7.2 Hz), 7.94 (d, 2H, J = 7.2 Hz); ^{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-phenyl-3,5-Dimethyl-4-chloropyrazol (table 2, entry 8). IR (ATR, neat): 1597, 1558, 1504, 1382, 1366, 1099, 1052, 761, 696 $Cm^{-1;}$ ^{1}H NMR (400 MHz, $CDCl_3$): 2.3(s, 3H), 7.38 (t,1H, J = 8 Hz), 7.41(d, 2H, J = 8), 7.48(t, 2H, J = 8 Hz). ^{13}C NMR(100 MHz, $CDCl_3$): 11.23, 11.8, 110, 124.96, 128.14, 129.56, 129.6, 136, 140, 146.46.

1-(4-bromophenyl)-3,5-dimethyl-4-chloropyrazole (table 2, entry 10).IR (ATR, neat): 1588, 1500, 1470, 1401, 1380, 1366, 1099, 1070. 1037, 1008, 831, 810, 795 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 2.33 (d, 6 H), 7.31 (d, 2H, J = 8.4 Hz), 7.6 (d, 2H, J = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.88, 11.39, 121.3, 125, 125.85, 132, 132.32, 138.79, 146.56. Anal. calcd. for $C_{11}H_{10}BrClN_2$: C, 46.26; H, 3.53; Br, 27.98; Cl, 12.41; N, 9.81. Found: C, 48.9; H, 3.3; Br and Cl, 37.8; N, 10.0.

1-(4-bromophenyl)-3,5-diphenylpyrazole(table 2, entry 11).IR (ATR, neat): 1590, 1546, 1491, 1457, 1399, 1362, 1209, 1063, 1010. 969, 831, 809, 764, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 6.84 (s, 1 H), 7.36 (m, 12H), 7.92 (d, 2 H, J = 8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): 105.73, 120.9, 125.8, 126.6, 128.2, 128.6, 128.7, 128.74, 128.8, 130.4, 132, 132.8, 139, 144, 153.

1-(4-methylphenyl)-3,5-diphenyl-pyrazole(table 2, entry 13). IR (ATR, neat): 1604, 1545, 1511, 1480, 1361, 972, 822, 760, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 2.38 (s, 3 H), 6.83 (s, 1 H), 7.16 (d, 2 H, J = 8.4 Hz), 7.30 (m, 8H), 7.44 (t, 2 H, J = 7.6 Hz) 7.93 (dd, 2 H, J = 7.8 Hz, J = 1.2 Hz). 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. ^{13}C-NMR (100 MHz, $CDCl_3$): 21.1, 105, 125.2, 125.8, 128, 128.2, 128.5, 128.6, 128.76, 129.5, 130.6, 133, 137.5, 137.7.

1-(4-methylphenyl)-3-methyl-5-phenyl-pyrazole(table 2, entry 14). IR (ATR, neat): 1607, 1550, 1513, 1444, 1365, 1025, 968, 818, 762, 707 Cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 2.35 (s, 3 H), 2.4 (s, 3 H), 6.3 (s, 1 H), 7.12 (d, 2 H, J = 8.4 Hz), 7.16 (d, 2 H, J = 8.4 Hz), 7.24 (m, 2 H), 7.3 (m, 3 H).

1-(4-methoxyphenyl)-3,5-diphenylpyrazole (table 2, entry 15). IR (ATR, neat): 1606, 1510, 1481, 1462, 1363, 1300, 1251, 1068, 1029, 846, 760, 691 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 3.9 (s, 3 H), 6.82 (s, 1 H), 6,9 (d, 2 H, J = 6.5 Hz), 7.3 (m, 8 H), 7.44 (m, 2 H), 7.93 (d, 2 H, J = 6.5 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): 55, 105, 114, 125.8, 126.7, 127.9, 128.2, 128.5, 128.6, 128.7.

1-(4-methoxyphenyl)-3-phenyl-5-methyl pyrazole (table 2, entry 16). IR (ATR, neat): 1607, 1571, 1514, 1250, 1030, 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 17). IR (ATR, neat): 1598, 1574, 1370, 1292, 1191, 1175, 1125, 968, 812, 757, 702, 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, 1 H), 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 18). IR (ATR, neat): 1594, 1557, 1484, 1458, 1379, 1191, 1174, 1101, 942, 759, 684, 658 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 2.1 (s, 3 H), 6.81 (s, 1H), 6.93 (d, 2 H, J = 7.8 Hz), 7.22 (m, 6H), 7.53 (d, 2 H, J = 7.8 Hz), 7.62 (m, 4 H).

1-(4- tolosulfono)-3(5)-phenyl-5(3)-methyl pyrazole(table 2, entry 19). IR (ATR, neat): 1593, 1563, 1459, 1375, 1294, 1278, 1190, 1122, 1076, 811, 767, 688, 670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 2.4 (s, 3 H), 2.6 (s, 3 H), 6.4 (s, 1 H), 7.32 (d, 2 H, J = 8.2 Hz), 7.4 (m, 3 H), 7.8 (d, 2 H, J = 6.8 Hz), 7.9 (d, 2 H, J = 8.2 Hz).

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