ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2016, *61*(2), 119-123

NANO-TiO_2: AN EFFICIENT AND REUSABLE CATALYST FOR THE SYNTHESIS OF 1,3,5-SUBSTITUTED PYRAZOLES

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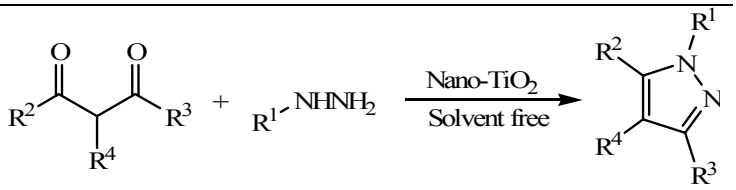
Received November 16, 2015

A Nano-TiO_2 is an efficient catalysis for the synthesis of 1,3,5-substituted pyrazoles via condensation of 1,3-diketones and hydrazines. Simple procedure, mild heating, solvent free, high yielding, and easy workup are some advantages of this protocol. The catalyst can be recovered easily and reused many times without significant loss in catalytic activity and selectivity.



INTRODUCTION

Titanium dioxide (TiO_2), a white pigment, is used as filler in rubber and plastics, in the manufacture of paint and surface coating on paper. Fine particles of TiO_2 scatter light so strongly that they can be used to produce films of high capacity. In addition, TiO_2 is chemically inert and its LD_{50} oral rat is upper 10000 mg⁄kg.[1] TiO_2 nanoparticles have been widely investigated in the past decades due to their multiple potential applications, such as catalytic activity for synthesis of 14-aryl or alkyl-14H-dibenzo[a,j] xanthenes,[2] *β*-acetamido ketones,[3] quinoxalines,[4] 2-Indolyl-1-nitroalkane,[5] 9-aryl-1,8-dioxo-octahydroxanthenes,[6] and α, α′-bis(substituted-benzylidene) cycloalkanone derivatives.[7]

Pyrazole derivatives have a wide range of biological activities. They can be used as anti-inflammatory,[8] antipyretic,[9] antidepressant,[10] antibacterial,[11] anticonvulsant,[12] antitumor,[13] antimicrobial,[14] anticancer,[15] antiviral,[16] antifungal[17] and antimalarial activity against.[18] They also serve as pesticides,[19] and insecticides.[20]

Generally, pyrazoles are synthesized by the two-component condensations of a 1,3-dicarbonyl derivative with a substituted hydrazine in the presence of an acidic catalyst,[21] such as Sulfuric acid,[22] zinc L-proline,[23] Scandium(III) triflate,[24] heteropolyacids,[25] amberlyst-70,[26] Phosphorus pentoxide supported on silica gel,[27] multi-SO_3H Brønsted acidic ionic liquid,[28] silica supported sodium hydrogen sulphate,[29] silica-supported sulfuric acid,[30] have been employed to affect this transformation. However, most of these methods often require relatively harsh reaction conditions such as high temperatures, expensive or highly acidic catalysts, and prolonged reaction times, there still remains the necessity of finding newer methods.

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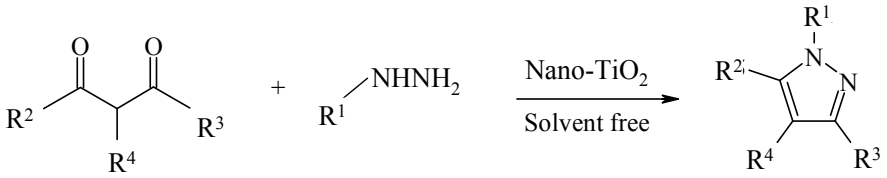
RESULTS AND DISCUSSION

In continuation of our investigations on the applications of nano-TiO_2 in organic synthesis, we have studied the synthesis of pyrazoles derivatives in the presence of it *via* condensation of 1,3-diketones and hydrazines. The reaction of phenylhydrazine (2mmol) with 1,3-diphenyl-1,3-propanedione (2 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 nano TiO_2, the reaction revealed that the best conditions were solvent-free at 60 °C and a molar ratio of 1,3-Diketone : hydrazine derivatives: nano TiO_2 of 2 : 2 : 0.4. Herein, we report that nano-TiO_2 is an efficient and reusable catalyst for the synthesis of pyrazoles derivatives and is comparable with some other applied catalysts (Table 1).

To study the reusability of the nano-TiO_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 9 and 10). The catalyst was reusable although a gradual decline was observed in the 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 1,3-diphenyl-1,3-propanedione under thermal conditions which gave 1-(2,4-dinitrophenyl)-3,5-diphenyl-pyrazole in 91% yield. 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 normal heating, (Scheme 1 and Table 2).



Scheme 1

Table 1

Optimization of the reaction conditions[a]

Entry	Catalyst (mol %)	Solvent	Time (min)	Condition	Yield (%) [b]
1	Nano TiO_2 (15)	Solvent-free	15	60 °C	73
2	Nano TiO_2 (20)	Solvent-free	15	60 °C	91
3	Nano TiO_2 (25)	Solvent-free	15	60 °C	92
4	Nano TiO_2 (20)	Solvent-free	10	60 °C	76
5	Nano TiO_2 (20)	Solvent-free	20	60 °C	93
6	Nano TiO_2 (20)	Solvent-free	15	rt	58
7	Nano TiO_2 (20)	Chloroform	15	Reflux	65
8	Nano TiO_2 (20)	Ethanol	15	Reflux	76
9	Nano TiO_2 (20) 2^{th} run	Solvent-free	10	60 °C	84
10	Nano TiO_2 (20) 3^{rd} run	Solvent-free	10	60 °C	80

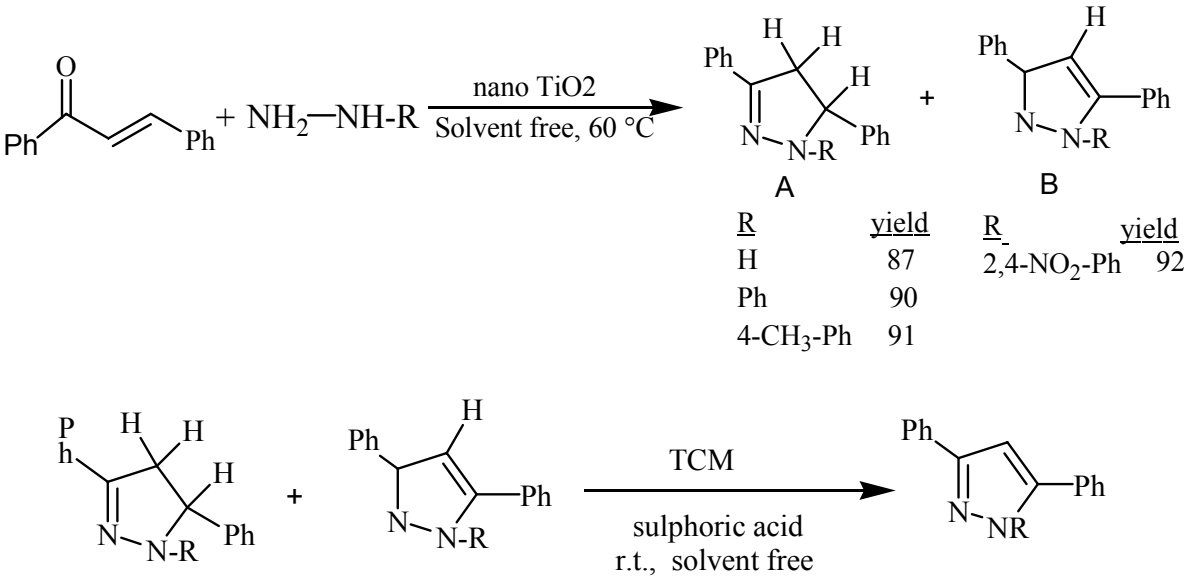
[a] phenylhydrazine (2 mmol) and 1,3-diphenyl-1,3-propanedione (2 mmol) were applied.
[b] Isolated pure yield.

Table 2

Synthesis of 1,3,5-substituted pyrazoles

Entry	R_1	R_3	R_4	R_5	Yield (%)[a]	Mp (°C)
1	C_6H_4	C_6H_5	H	C_6H_5	92	137-138
2	2- Cl-C_6H_4	C_6H_5	H	C_6H_5	89	126-127
3	2,4- O_2N-C_6H_4	C_6H_5	H	CH_3	89	128-130
4	H	C_6H_5	H	CH_3	75	203-205
5	4- Br-C_6H_4	CH_3	Cl	CH_3	83	87-88
6	2,4- O_2N-C_6H_4	CH_3	Cl	CH_3	86	167-168
7	4- Br-C_6H_4	C_6H_5	H	C_6H_5	90	117-119
8	C_6H_4	C_6H_5	H	CH_3	84	55 -57
9	4- Me-C_6H_4	C_6H_5	H	C_6H_5	89	104-105
10	C_6H_4	CH_3	Cl	CH_3	92	oil
11	2,4- O_2N-C_6H_4	C_6H_5	H	C_6H_5	91	149-150
12	H	C_6H_5	H	C_6H_5	79	200-201
13	2,4- O_2N-C_6H_4	CH_3	H	CH_3	82	121-122

[a] Isolated pure yield.



Scheme 2

Dihydropyrazole produced by the condensation of hydrazine with chalcone A. In this case, tautomer A is more stable than B because the bonding energy of C=N is higher than C=C. Dihydropyrazole A produced by the condensation of phenyl hydrazine or 4-methyl phenyl hydrazine. In these materials, the nucleophilicity of NH is higher than that of NH_2 but in the 2,4-dinitrophenyl hydrazine NH_2 is higher than NH in the Michael addition and produced dihydropyrazole B.

The 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 analyser was done by Costech ECS 4010 CHNS-O analyser. Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus.

EXPERIMENTAL

General procedure for the synthesis of pyrazole derivatives

A mixture of 1,3-diketone (2 mmol), hydrazine derivatives (2 mmol) and nano TiO_2 (20%) was heated 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 pyrazoles derivatives in 75-92 % yields.

General procedure for the synthesis of pyrazole via condensation of chalcones and hydrazine

A mixture of chalcones (2 mmol), hydrazine derivatives (2 mmol) and nano TiO_2 (20%) was heated at 60 °C. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was added TCM (2 mmol) and sulphuric acid (0.2 mL). The reaction mixture was stirred vigorously at room temperature for 3 h. 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 pyrazoles derivatives.[31]

1,3,5-triphenyl-pyrazole (**1**)

FT-IR (ATR, neat) 1594, 1495, 1455, 1362, 971, 920, 814, 764, 693 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 6.84 (s, 1 H), 7.40 (m, 13H), 7.97 (d, *J*= 8.4 Hz, 2 H). ^{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-(2-chlorophenyl)-3,5-diphenyl-pyrazole (**2**)

FT-IR (ATR, neat): 1598, 1543, 1488, 1458, 1360, 1212, 1074, 971, 806, 757, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 6.90 (s, 1 H), 7.45 (m, 12 H), 7.94 (d, *J*= 8.4 Hz, 2 H).

1-(2,4-dinitrophenyl)-3-phenyl-5-methyl-pyrazole (**3**)

FT-IR (ATR, neat): 1609, 1538, 1505, 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.

3-Phenyl-5-methyl-1H-pyrazole (**4**)

FT-IR (ATR, neat): 2400-3400, 1613, 1595, 1465, 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 $C_{10}H_{10}N_2$: 4.53; H, 3.06; Cl, 11.92; N, 18.89; O, 21.57. Found: C, 46.6; H, 3.0; N, 18.7.

1-(4-bromophenyl)-3,5-dimethyl-4-chloropyrazole (**5**)

FT-IR (ATR, neat): 1588, 1501, 1470, 1401, 1380, 1366, 1100, 1071. 1037, 1008, 831, 810, 795 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): 2.32 (s, 3 H), 2.33 (s, 3 H), 7.31 (d, *J*= 8.6 Hz 2H), 7.6 (d, *J*= 8.6 Hz, 2 H,); 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-(2,4-dinitrophenyl)-3,5-dimethyl-4-chloropyrazole (**6**)

FT-IR (ATR, neat): 1614, 1531, 1425, 1342, 1133, 1105, 1029, 904, 833, 743 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 2.3 (s,

6 H), 7.70(d, *J*= 10.5 Hz, 1H), 8.57 (dd, *J*= 10.5 and 3.4 Hz, 1 H), 8.83 (d, *J*= 3.4 Hz, 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, Found: C, 46.6; H, 3.0; N, 18.7.

1-(4-bromophenyl)-3,5-diphenyl-pyrazole (**7**)
FT-IR (ATR, neat): 1588, 1546, 1491, 1457, 1399, 1362, 1209, 1063, 1010. 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);

1,3-Phenyl-5-methyl-pyrazole (**8**)
FT-IR (ATR, neat): 1596, 1457, 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-(4-methylphenyl)-3,5-diphenyl-pyrazole (**9**)
FT-IR (ATR, neat): 1598, 1511, 1462, 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, *J*= 8.4 Hz, 2 H), 7.30 (m, 6H), 7.44 (t, *J*= 8.4 Hz, 2 H,) 7.93 (d, *J*= 8.4 Hz, 2 H,); ^{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. 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-Phenyl-3,5-dimethyl-4-chloropyrazole (**10**)
FT-IR (ATR, neat): 1597, 1504, 760, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): 2.31 (s, 3 H, CH_3), 2.32 (s, 3H, CH_3), 7.38-7.42 (m, 3 H), 7.45-7.49 (m, 2 H); ^{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.

3,5-diphenyl-1H-pyrazole (**12**)
FT-IR (ATR, neat) 1605, 1461, 1316, 1181, 1075, 1000, 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.

3,5-Diphenyl-4,5-dihydro-1H-pyrazole (A, R=H):
FT-IR (ATR, neat): 1590, 1490, 744, 690 cm^{-1}; ^{1}H-NMR(400 MHz, $CDCl_3$):3.16(dd, *J*= 16.8 and 7.2 Hz, 1H), 3.86(dd, *J*= 16.8 and 12.4 Hz, 1H), 5.29 (dd, *J*= 12.4 and 7.2 Hz, 1H), 6.81(t, *J*= 7.8 Hz, 1H), 7.10(d, *J*= 7.8 Hz, 2H), 7.22(t, *J*= 7.8 Hz, 2H), 7.35 (1H, NH), 7.40(t, *J*= 7.6 Hz, 3H), 7.74(d, *J*= 7.6 Hz, 2H)

1,3,5-Triphenyl-4,5-dihydro-1H-pyrazole (A, R=Ph):
FT-IR (ATR, neat): 1596, 1393, 745, 691 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$):3.16(dd, *J*= 12.4 and 7.6 Hz, 1H), 3.86(dd, *J*= 12.4 and 14.4 Hz, 1H), 5.29(dd, *J*= 7.6 and 14.4 Hz, 1H), 6.66(s, 1H), 7.64(s, 2H), 6.77-7.75(m, 12H).

1-(2,4-Dinitro-phenyl)-3,5-diphenyl-2,3-dihydro-1H-pyrazole (**B**):
FT-IR (ATR, neat): 3104, 1609, 1587, 1446, 716, 690 cm^{-1}; ^{1}H-NMR(400 MHz, $CDCl_3$): 7.12(d,*J*= 16.8 Hz, 1H), 7.17(d, *J*= 16.8 Hz, 1H),7.36(t, *J*= 9.8 Hz, 1H), 7.46(t, *J*= 12.4 Hz, 2H), 7.52(t, *J*= 12.4 Hz, 2H), 7.61(d, *J*= 7.2 Hz, 2H), 7.67(t, *J*= 7.2 Hz, 1H), 7.79(d, *J*= 8.6 Hz, 2H), 8.14(dd, *J*= 9.6 and 2.5 Hz, 1H), 8.37(dd, *J*= 9.6 and 2.5 Hz, 1H), 9.18(d, *J*= 2.5 Hz, 1H), 11.81(1H, NH).

CONCLUSIONS

In conclusion, we have demonstrated a simple method for the synthesis of pyrazoles using Nano TiO_2 as an eco-friendly, reusable and efficient catalyst. Short reaction times, high yields, scale-up, clean process, simple methodology, easy work-up, and green conditions are the advantages of this protocol.

Acknowledgements: The Research Council of Yazd University is gratefully acknowledged for the financial support for this work.

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