RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2014, **4**, 61193

Cellulose sulfuric acid as a bio-supported and efficient solid acid catalyst for synthesis of pyrazoles in aqueous medium

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Received 4th October 2014
Accepted 6th November 2014

DOI: 10.1039/c4ra11440j

www.rsc.org/advances

A convenient and practical method was described for the regioselective synthesis of pyrazoles from hydrazines/hydrazides and 1,3-dicarbonyl compounds *via* the Knorr synthesis in water with cellulose sulfuric acid (CSA) as a biopolymer-based solid acid catalyst. Various hydrazines and hydrazides were reacted with 1,3 diketones and the desired pyrazoles were obtained in high yields. The reaction of less reactive hydrazines with 1,3-dicarbonyl compounds stopped at the corresponding hydrazone derivatives. Hydrazides were employed with β-ketoester, and imine adducts were the only isolated product. Simple isolation of products, mild reaction conditions, reusability of solid acid catalysts and short reaction times are advantages of this green procedure.

Introduction

Heterogeneous catalysts have recently attracted much attention for the synthesis of fine chemicals from both environmental and economical perspectives. The use of solid acids produces one of the most promising green, sustainable processes in organic synthesis.[1] From the current point of view, cellulose is the most common organic polymer on earth and is considered as an almost inexhaustible source of raw materials to meet the increasing demand for environmentally-friendly and biocompatible products. The unique properties of cellulose and derivatives have been the subject of intense research for more than 100 years, marked by frequent controversy over the results, making them attractive alternatives for conventional synthetic organic or inorganic supports for catalytic applications.[2] The most frequently synthesized and commonly used cellulose derivatives with functionalization patterns of high uniformity are particularly important with new properties and applications. A considerable stimulation of scientific and technological research has been triggered over the past 10 years in response to the growing global importance of renewable resources and environmentally compatible materials.[3] In the field of natural biopolymers, cellulose could especially be utilized as a support for catalytic applications.

Since a great amount of waste in the environment is attributed to the use of organic solvents,[4,5] there is a strong interest in the development of organic reactions in environmentally-friendly media.[6] Recently, water has been shown to induce unique reactivity and selectivity which cannot be attained for reactions in organic media. In addition, water as a solvent will reduce the use of harmful organic solvents and may lead to the development of environmentally-friendly chemical processes.[7–15] Therefore, water as a reaction medium would be highly desirable if such reactions could be performed using reusable catalysts.

In the past decade, pyrazoles have emerged as a significant class of nitrogenated heterocycles that have attracted a great deal of interest due to the discovery of the considerable properties exhibited by a great number of their derivatives. A number of them represent an important class of compounds that find extensive use in the pharmaceutical industry.[16,17]

Compounds containing a pyrazole motif are being developed in a wide range of therapeutic areas, including metabolic and oncological diseases.[18–24] To date, a number of pyrazole-containing compounds have been successfully commercialized, such as sildenafil ((a); Viagra), rimonabant ((b); Acomplia) and celecoxib ((c); Celebrex)[25–27] (Fig. 1).

Moreover, some pyrazoles have attracted considerable attention in supramolecular and polymer chemistry, herbicides, the food industry, and as cosmetic colourings and UV stabilizers, while some have liquid crystal properties.[28–33] Substituted pyrazole derivatives have also been used as ligands for transition-metal-catalyzed cross-coupling reactions.[34–36] Accordingly, the agrochemical, pharmaceutical and chemical industries have a great interest in the synthesis of pyrazoles.

By far, the two most prevalent strategies that have been developed for constructing pyrazole rings are the classic Knorr pyrazole synthesis in the presence of Brønsted or Lewis acids,[37–39] and 1,3-dipole cycloaddition of diazoalkanes or nitrile imines with olefins or alkynes.[40–42]

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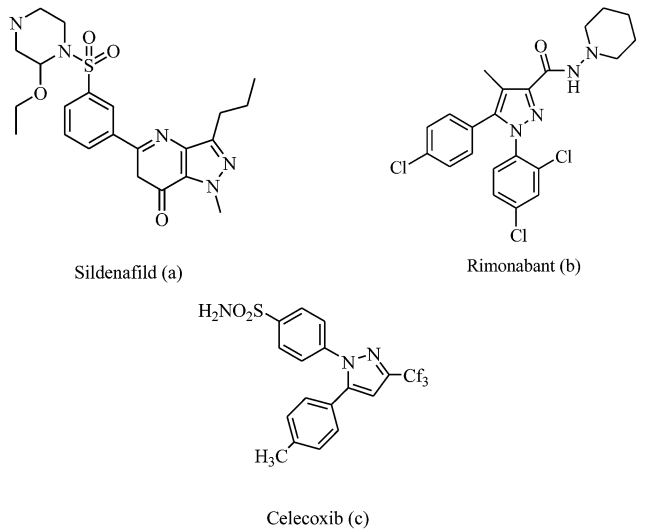


Fig. 1 Biologically active compounds with a pyrazole substructure.

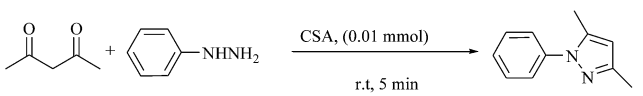
In this paper, we report the regioselective perpetration of pyrazoles by condensation of hydrazines/hydrazides with various compounds including 1,3-diketones and β-ketoesters, *via* the Knorr synthesis using CSA as an efficient, reusable, and environmentally friendly heterogeneous acidic catalyst at room temperature in pure water.[43–45]

Experimental

General

Chemicals were purchased from Merck and Fluka chemical companies. The IR spectra were run on a Perkin Elmer 780 spectrophotometer in KBr pellets and reported in cm^{-1}. ^{1}HNMR spectra were recorded on a Bruker Avance DPX-250 MHz spectrometer using TMS as an internal standard and $CDCl_3$ or DMSO as solvent. ^{13}CNMR spectra were recorded on a Bruker Avance DPX-62.5 MHz spectrometer ($CDCl_3$ or DMSO solution). Mass spectra were recorded on GC 17A, MS QP 5050 Shimadzu. Elemental analysis for C, H and N were obtained using an Elementar, Vario EL III. All the reactions were monitored by thin-layer chromatography (TLC) on pre-coated sheets of silica gel G/UV-254 using UV light for visualization. Melting points were determined with Electrothermal 9100 melting point apparatus.

Table 1 Cellulose sulfuric acid catalyzed condensation of pentane-2,4-dione and $PhNHNH_2$ in different solvents[a]



Entry	Solvent	Yield[b] (%)
1	EtOH	96
2	MeCN	92
3	CH_2Cl_2	92
4	EtOAC	93
5	THF	92
6	H_2O	94

[a] Reactions were performed with pentane-2,4-dione (1 mmol), $PhNHNH_2$ (1 mmol) and CSA (0.01 mmol H^+) in solvent (2 mL) by stirring the mixture for 5 min at r.t. [b] Isolated yields after column chromatography.

Preparation of cellulose sulfuric acid

Cellulose sulfuric acid was prepared and characterized according to the known procedures.[43,44] To a magnetically stirred mixture of 5.0 g of cellulose in 20 mL of chloroform, chlorosulfonic acid (1.0 g, 9 mmol) was added dropwise at 0 °C over 2 h. HCl gas was removed from the reaction vessel immediately. After the addition was complete, the mixture was stirred for 2 h. Then, the mixture was filtered and washed with 30 mL of chloroform and dried at room temperature to yield 5.25 g of cellulose sulfuric acid as a white powder. Sulfur content of the samples determined by conventional elemental analysis was 0.55 mmol g^{-1} for cellulose sulfuric acid. The number of H^+ sites on the cellulose–SO_3H determined by acid–base titration was 0.50 mmol g^{-1}, which was very close to the sulfur content. These results indicated that most of the sulfur species on the sample were in the form of sulfonic acid groups.

General procedure for the preparation of pyrazol derivatives

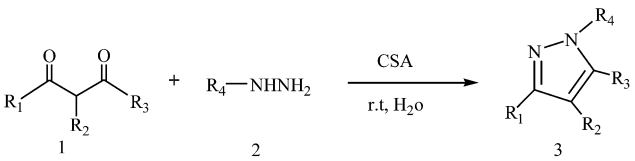
A mixture of 1,3-diketone (1 mmol), cellulose sulfuric acid (0.02 g) and hydrazines/hydrazides (1 mmol) in 2 mL water was stirred at r.t. for the given time (Tables 2 and 3). The products were then extracted with ethyl acetate (3 × 5 mL) and washed with dilute sodium bicarbonate solution. After drying the organic layer over sodium sulphate, the solvent was removed under vacuum. The products thus obtained were pure enough for most purposes, as indicated by ^{1}H NMR spectra, but a few of them were purified by column chromatography (EtOAc–hexane: 1 : 10). All products were identified by comparison of analytical data (IR, NMR, MS and CHN) with those reported for authentic samples.[46–49]

Results and discussion

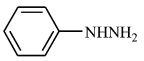
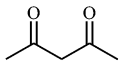
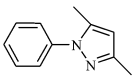
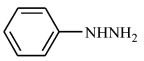
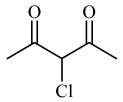
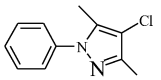
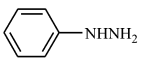
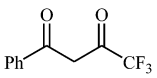
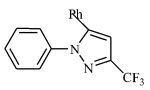
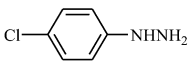
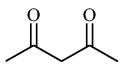
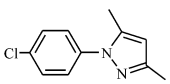
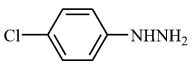
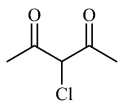
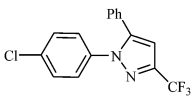
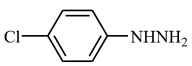
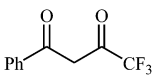
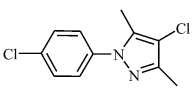
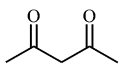
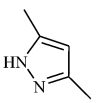
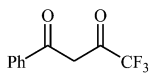
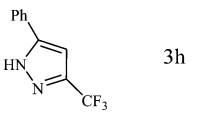
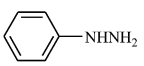
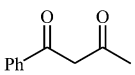
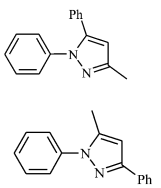
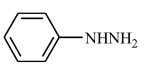
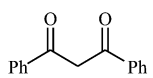
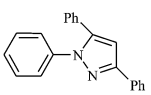
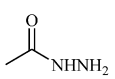
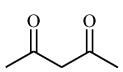
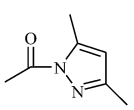
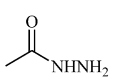
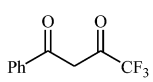
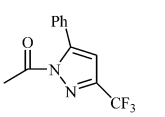
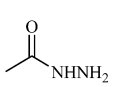
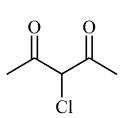
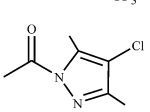
Initially, the condensation of hydrazines/hydrazides with 1,3-dicarbonyl compounds in the presence of CSA was examined. As a model study, we chose the condensation partners pentane-2,4-dione (1 mmol) and $PhNHNH_2$ (1 mmol) with the catalyst CSA (0.02 g equal to 0.01 mmol H^+) as a system, and different solvents including EtOH, MeCN, CH_2Cl_2, EtOAC, THF and H_2O were tested, as well as the solvent free condition. As summarized in Table 1, the yield of the condensation was excellent in water, and approximately equal to those of the reactions in the above organic solvents.

It is interesting to note that, although the solvent free conditions were the same as the conditions using H_2O for condensation of phenyl hydrazine with pentane-2,4-dion (entry 1) from the point of view of reaction time and yield, the condensation of thiophencarboxylic acid hydrazide with pentane-2,4-dion (entry 17) to the corresponding pyrazole did

Table 2 Regioselective synthesis of pyrazoles catalyzed by CSA as a Brønsted acid at room temperature in water[a]



1 2 3

Entry	Hydrazine/hydrazide	1,3-Diketone	Time (min)	Product		Yield[b] (%)
1			4		3a	95
2			5		3b	75
3			4		3c	90
4			4		3d	94
5			6		3e	78
6			5		3f	92
7	NH_2NH_2		4		3g	93
8	NH_2NH_2		4		3h	93
9			8		3i	92[c]
10			12		3j	54
11			10		3k	85
12			10		3l	88
13			12		3m	72

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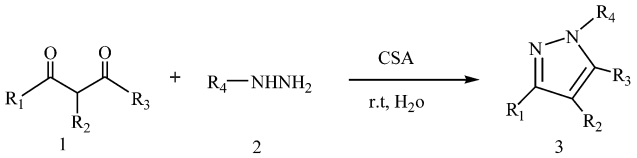
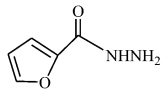
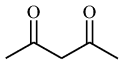
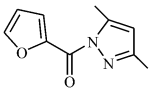
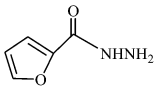
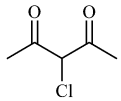
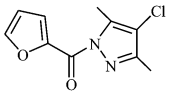
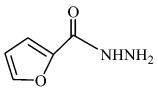
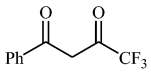
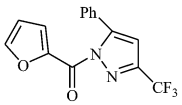
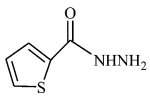
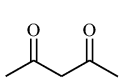
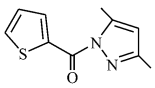


Entry	Hydrazine/hydrazide	1,3-Diketone	Time (min)	Product		Yield[b] (%)
14			12		3n	86
15			15		3o	70
16			10		3p	87
17			10		3q	88

[a] Reactions were performed with the 1,3-diketone (1 mmol), hydrazine/hydrazide (1 mmol) and CSA (0.02 g equal to 0.01 mmol H^+)in pure H_2O (2 mL) at r.t. [b] Isolated yields after column chromatography. [c] The regioisomers were formed in a ratio of 20 : 1.

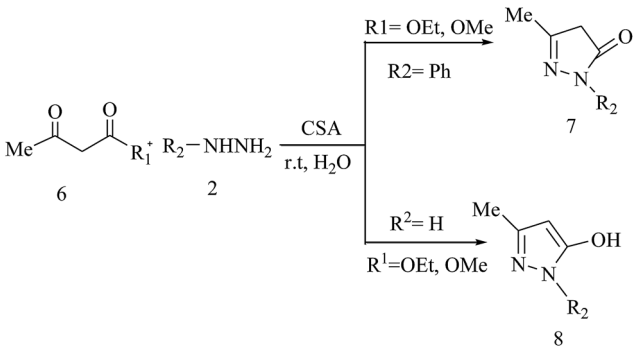
not proceed after 60 min. Further experiments revealed the optimum amount of catalyst to be 0.02 g equal to 0.01 mmol H^+.

After determining the optimum reaction conditions, we turned our attention to studying the scope of this method. Therefore, we reacted 1,3-diketones with hydrazines or hydrazides under mild reaction conditions. The results are summarized in Table 2. In all cases, the reaction proceeded readily at room temperature to produce the corresponding pyrazoles in good to excellent yields (72–94%). Various hydrazines (entries 1–10) and hydrazids (entries 11–17) reacted with 1,3 diketones and the desired pyrazoles were obtained in high yields. In view of the exceptional biological properties of heterocyclic hydrazides, a wide variety of heterocyclic hydrazides (entries 14–17) were evaluated, providing a convenient and flexible method for the synthesis of pyrazoles and encompassing heterocycles such as furan and thiophene as a functional arm at the 1-position, which may be useful for chemical entities in drug discovery. When an unsymmetrical diketone, 1-phenylbutane-1,3-dione, was employed to react with $PhNHNH_2$, two regioisomers were obtained in the ratio of 20 : 1 (Table 2, entry 9). In the case of the

Table 3 The reaction of β-diketones and β-ketoesters with hydrazines or hydrazides

Entry	Hydrazines/hydrazides	R^1	Product	Time (min)	Yield[a,b] (%)
1	Phenyl hydrazine	OMe	**7a**	8	92
2	Phenyl hydrazine	OEt	**7b**	6	93
3	Hydrazine	OMe	**8a**	6	94
4	Hydrazine	OEt	**8b**	5	94
5	2,4-Dinitrophenylhydrazine	Me	**10a**	5	93[c]
6	2,4-Dinitrophenylhydrazine	OMe	**11a**	6	90
7	2,4-Dinitrophenylhydrazine	OEt	**11b**	6	92
8	Acetohydrazide	Me	**13a**	5	94
9	2-Furancarboxylic acid hydrazide	Me	**13b**	6	93
10	Acetohydrazide	OMe	**14a**	8	88
11	Acetohydrazide	OEt	**14b**	6	89
12	2-Furancarboxylic acid hydrazide	OMe	**14c**	8	85

[a] Reaction conditions: nucleophile (1 mmol) β-diketone/β-ketoester (1 mmol), CSA (0.02 g equal to 0.01 mmol H^+) water (2 mL). [b] The yield refers to pure isolated product. [c] Nucleophile 2 mmol.

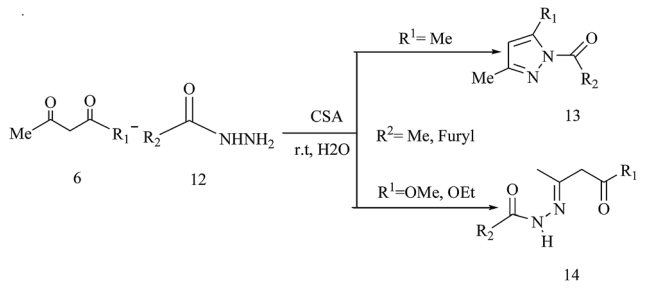


Scheme 1 Comparison of hydrazine/phenylhydrazine in the reaction with β-ketoester.

reaction between 1,3 diphenyl propane-1,3-dione and phenyhydrazine, low activity of the carbonyl group due to the conjugative effect of the aromatic ring that stabilized the enol-tautomer caused the yield to reduce to 54% (entry 10). It is noteworthy that the desired product was obtained in a very low yield in the absence of the catalyst even after 1 h (20%).

β-ketoesters (ethyl acetoacetate and methyl acetoacetate) reacted readily with phenyl hydrazine or hydrazine hydrate under the same conditions to form compounds **7** and **8**, respectively (Scheme 1), in excellent yields. Compound 7 exists in the keto-form (9% enol-form was obtained) (Scheme 1; Table 3, entries 1–2), and compound **8** is in the enol-form, as identified by their respective NMR and IR spectra (Scheme 1; Table 3, entry 3 and 4).

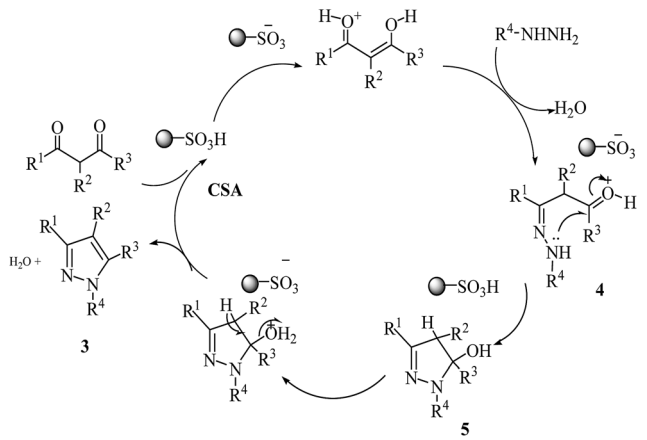
Following this procedure, the reaction of less reactive hydrazines with 1,3-dicarbonyl compounds was tested. The condensation of 2,4-dinitrophenylhydrazine (**9**) with diketone or β-ketoester stopped at the corresponding hydrazone derivatives (Scheme 2; Table 3, entries 5–7). The low reactivity of 2,4-dinitrophenylhydrazine containing electron-withdrawing groups (NO_2) can be attributed to the groups' relatively weak nucleophilicity and, therefore, the activity in this reaction decreased. The use of stoichiometric quantities (1 : 1) of 2,4-dinitrophenylhydrazine and diketone gave product **10** in 40% yield relative to the diketone. Treatment of diketone (1 eq.) with of 2,4-dinitrophenylhydrazine (2 eq.) improved the yield to 93%.



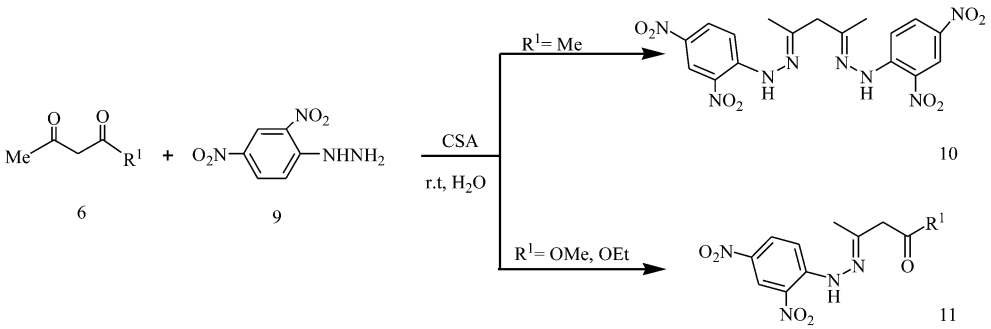
Scheme 3 Reaction of methyl/furyl hydrazide with dicarbonyl compounds.

When hydrazides were employed with β-ketoester, the reaction did not yield any pyrazole products and the imine adducts were the only isolated product (Scheme 3; Table 3, entries 10–13). Nevertheless, diketones led to the desired pyrazole in an excellent yield (Table 3, entries 8–9).

The proposed mechanism for the formation of the products can be explained by the pathway presented in Scheme 4. It is conceivable that, due to the better enolizeability of one of the carbonyl groups relative to the other, the terminal nitrogen of hydrazine/hydrazide.initially attacks the more electrophilic carbon. So, the first step involves a facile enolization/imination



Scheme 4 Suggested mechanism for the synthesis of pyrazole in the presence of CSA.



Scheme 2 Condensation of 2,4-dinitrophenylhydrazine with diketones and β-ketoester.

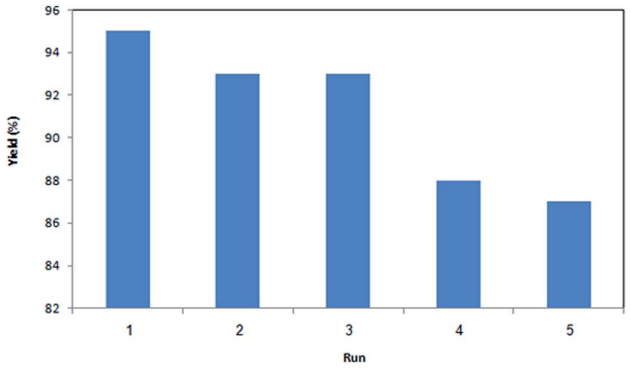


Fig. 2 Reusability of catalyst in condensation of pentane-2,4-dione and $PhNHNH_2$. Reaction time = 4 min.

reaction activated by the catalyst CSA, which results in intermediate **4**. Intramolecular nucleophilic addition in **4** catalysed by CSA gives **5**. Finally, dehydration of **5** in the presence of the catalyst produces the corresponding pyrazole **3** and releases the catalyst for the next catalytic cycle.[50]

Recyclability of the catalyst was also examined. To this end, the catalyst which was recovered from the reaction between pentane-2,4-dione and $PhNHNH_2$ by filtration was washed three times with DCM and dried at 80 °C for period of 6 h in a vacuum oven. The recovered catalyst can be reused four times in subsequent reactions without any significant loss in its activity. The results with the recyclable CSA are summarized in Fig. 2.

Conclusion

In summary, cellulose sulfuric acid, an efficient, non-toxic, reusable and solidly supportive biodegradable acid catalyst, has been prepared and utilized for the synthesis of pyrazole derivatives by a one-pot coupling reaction of dicarbonyl compounds and hydrazines/hydrazides. Moreover, the broad scope, operational simplicity, practicability, and mild reaction conditions render it an attractive approach for the generation of different compounds with potential properties for use in medicinal chemistry programmes.

Selected experimental data

3,5-Dimethyl-1-phenyl-1*H*-pyrazole (3a). Orange colour liquid, yield 93%. IR (KBr): 3055, 2981, 2959, 2910, 2861, 1597, 1546, 1492, 1420, 1381, 1366, 1131, 1072, 1020, 977, 911, 779, 755, 690 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.29 (s, 6H, $2CH_3$), 5.99 (s, 1H, CH), 7.34 (m, 5H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$): d 12.4, 13.5, 106.9, 124.7, 127.2, 129.0, 139.4, 139.9, 148.9. MS (EI, 70 eV) *m*/*z* (%): 172(M^+, 38), 130(20), 118(18), 105(28), 91(18), 77(100), 65(25), 56(18), 51(48), 43(67). Anal. calcd for $C_{11}H_{12}N_2$ (%): C, 76.71; H, 7.02; N, 16.27. Found: C, 76.58; H, 7.15; N, 16.32.

5-Phenyl-3-(trifluoro methyl)-1*H*-pyrazole (3h). White solid, (93%, 0.197 g), mp: 121–122 °C (Lit.[49] 120–121 °C). IR (KBr): 3298, 3075, 2974, 1638, 1565, 1492, 1443, 1335, 1246, 1160, 1129, 1063, 1026, 752, 685 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ = 6.72 (s, 1H, CH), 7.38–7.45 (m, 3H, Ph), 7.50–7.63 (m, 2H, Ph), 8.00 (br, 1H, NH). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 101.1, 125.6, 127.9, 129.2, 129.4, 143.2, 143.8, 145.2. MS (EI, 70 eV) *m*/*z* (%): 213(M + 1, 4), 212(M^+, 33), 77(62.4), 69(16.5), 50(31.6). Anal. calcd for $C_{10}H_7F_3N_2$ (%): C, 56.61; H, 3.33; N, 13.20. Found: C, 56.73; H, 3.28; N, 13.08.

1-(2-Furoyl)-3,5-dimethyl-1*H*-pyrazole (3n). White solid, (86%, 0.163 g), mp: 105–106 °C. IR (KBr): 3125, 3100, 2990, 2930, 1680, 1585, 1565, 1460, 1375, 1350, 1275, 1025, 950, 875 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 2.10 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 5.83 (s, 1H, CH), 6.39 (dd, 1H, CH), 7.52 (d, 1H, CH), 7.74 (d, 1H, *J* = 3 Hz, CH). MS (EI, 70 eV) *m*/*z* (%): 191(M + 1, 8.7), 190(M^+, 33.5), 161(100), 133(28.9), 108(24.5), 94(54). Anal. calcd for $C_{10}H_{10}N_2O_2$ (%): C, 63.15; H, 5.30; N, 14.73. Found: C, 63.45; H, 5.26; N, 15.18.

5-Methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (7a). White solid, (92%, 0.160 g) mp: 127–128.5 °C (Lit.[46] 127–129 °C). IR (KBr): 3050, 2920, 1750, 1585, 1490, 1440, 1380, 1350, 1170, 1140, 910, 810, 760, 750, 680, 640 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ = 2.19 (s, 3H, CH_3), 3.42 (s, 2H, CH_2), 7.18 (m, 1H, Ph) 7.37 (m, 2H, Ph) 7.78 (m, 2H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 17.1, 43.1, 118.9, 125.1, 128.8, 138.0, 156.4, 170.6. MS (EI, 70 eV) *m*/*z* (%): 175(M + 1, 4.8), 174(M^+, 50), 149(4), 145(6), 142(2), 132(7), 105(26), 91(58), 77(100), 63(41), 50(65), 41(43). Anal. calcd for $C_{10}H_{10}N_2O$ (%): C, 68.95; H, 5.79; N, 16.08. Found: C, 68.42; H, 5.42; N, 15.88.

3-Methyl-1*H*-pyrazol-5-ol (8a). White solid, (94%, 0.092 g) mp: 220–222 °C (220–224 °C, CAS no. 108-26-9). IR (KBr): 2200–3400, 1620, 1564, 1457, 1250, 1195, 985, 765 cm^{-1}. ^1H NMR (250 MHz, DMSO) δ = 2.07 (s, 3H, CH_3), 5.2 (s, 1H), 10.3 (br, 2H, NH and OH). ^{13}C NMR (62.9 MHz, DMSO) δ = 11.5, 89.4, 140.2, 161.6. MS (EI, 70 eV) (*m*/*z*, (%): 99(M + 1, 5), 98(M^+, 100), 81(1), 69(15), 67(16), 56(12), 40(30). Anal. calcd for $C_4H_6N_2O$ (%): C, 48.97; H, 6.16; N, 28.56. Found: C, 49.09; H, 6.03; N, 28.38.

Ethyl-3-[(2,4-dinitrophenyl)hydrazono]butanoate (11a). Light orange solid, (90%, 0.279 g), mp: 88–89 °C (Lit.[47] 88–90 °C). IR (KBr): 3312, 3100, 2985, 1727, 1620, 1596, 1517, 1425, 1365, 1340, 1313, 1278, 1255, 1209, 1180, 1100, 1086, 1030, 920, 837, 743 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ = 1.28 (t, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.48 (s, 2H, CH_2), 4.24 (q, 2H, CH_2), 7.9 (d, 1H, Ar), 8.28 (dd, 1H, Ar), 9.10 (d, 1H, Ar), 11.10 (s, 1H, NH). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 14.2, 16.2, 44.8, 61.5, 116.6, 123.4, 129.2, 130.0, 138.3, 145.0, 150.8, 169.3. MS (EI, 70 eV) *m*/*z* (%): 310(M^+, 5), 279(2), 264(3), 237(5), 219(12), 196(7), 173(5.6), 167(8), 149(34), 131(14), 115(22), 103(25), 90(29), 76(46), 57(44), 41(100). Anal. calcd for $C_{12}H_{14}N_4O_6$ (%): C, 46.45; H, 4.55; N, 18.06. Found: C, 45.96; H, 4.39; N, 18.37.

Ethyl-3-(acetyl hydrazono)butanoate (14a). White solid, (88%, 0.164 g), mp: 88–90 °C (Lit.[48] 89 °C). IR (KBr): 3190, 2980, 2930, 1725, 1680, 1460, 1380, 1330, 1260, 1190, 1120, 1030, 870, 730, 620 cm^{-1} ^{1}HNMR (250 MHz, $CDCl_3$) δ = 1.24 (t, *J* = 7.3 Hz, 3H, CH_3), 1.92 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.26 (s, 2H, CH_2), 4.13 (q, 2H, *J* = 7.3 Hz, CH_2), 9.33 (s, 1H, NH). MS (EI, 70 eV) *m*/*z* (%): 187(M + 1, 1), 186(M^+, 10), 171(2), 144(9), 113(3), 98(100), 70(28), 57(11.0), 54(11), 42(26). Anal. calcd for $C_8H_{14}N_2O_3$ (%): C, 51.60; H, 7.58; N, 15.04. Found: C, 51.64; H, 7.55; N, 15.09.

Acknowledgements

We are thankful to the University of Birjand Research Council for the support of this work.

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