NbCl₅-AgClO₄ AS AN EFFECTIVE, SYNERGETIC CATALYTIC SYSTEM FOR THE SYNTHESIS OF FULLY SUBSTITUTED PYRAZOLES

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ABSTRACT

The synergetic effect of the combined catalytic system of NbCl₅-AgClO₄ has been observed for the one-pot synthesis of fully substituted pyrazoles through the pseudo-five-component reaction between aldehydes, phenyl hydrazine and ethyl acetoacetate at room temperature in dichloromethane. This approach exploited the synthetic potential, synergetic effect of the combined catalytic system over the constituent parts and offered many advantages such as excellent yields, shorter reaction times, easier isolation of products, and environmentally benign reaction conditions. A diverse range of aldehydes smoothly underwent the reaction under the optimized conditions to offer the corresponding products.

Keywords: Fully Substituted Pyrazoles, Niobium Pentachloride, Silver Perchlorate, Combined Catalytic System.

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INTRODUCTION

Green chemistry demonstrates the most preferred way of the current chemical research to develop efficient, sustainable, and environmentally benign synthetic methodologies.^{1,2} Multicomponent reactions (MCRs) have been acknowledged as a potent tool for the practical creation of chemical libraries of drug-like compounds with high levels of molecular diversity.^{3,4} Microwave-assisted organic synthesis (MAOS) is nowadays employed for the rapid and reliable production of chemical entities.⁵ Thus, multicomponent procedures employing combined catalytic systems are particularly welcomed due to their intrinsic advantages,⁶ to shift the conventional paradigm to green methodologies.

Transition metal-catalyzed carbon-carbon and carbon-heteroatom bond formations via multicomponent reactions are of most importance in organic synthesis,⁷ because of their high reactivity, selectivity, and mild reaction conditions. One of these is Niobium pentachloride (NbCl₅), a strong Lewis acid, has recently been recognized as a useful reagent in organic synthesis because of its high stability, low hygroscopic characteristics and ease of handling as compared to other Lewis acids. Some examples of organic transformation promoted by NbCl₅ have been reported, where its stoichiometric amount has been used.⁸ Moreover, the catalytic use of NbCl₅ in the acylative cleavage of ethers⁹ and C-P bond formation¹⁰ has been published. Quite recently, a highly selective dealkylation of alkyl aryl ethers with a stoichiometric amount of NbCl₅¹¹ has been reported. Friedel-Crafts acylation, one of the most fundamental reactions in organic synthesis¹²⁻¹⁴ has been found to catalyze by NbCl₅ and solved some severe environmental problems caused due to mineral or Lewis acid promoted acylation in the chemical industry.

Heterocycles are omnipresent in pharmaceuticals, natural products, and numerous organic functional molecules. Therefore, the development of a new, versatile, and efficient synthetic protocol for the

heterocycles has always been enthusiastic in the synthetic community.¹⁵ The pyrazole core is a privileged heterocyclic scaffold,¹⁶ and is a constituent of agrochemicals,¹⁷ and polymeric materials,¹⁸ besides its use as a unique ligand.¹⁹ Although pyrazoles are rarely found in natural products, they represent an important motif of man-made biologically active compounds such as celecoxib, fipronil, lonazolac, viagra, and many others.²⁰ The most popular methods for the preparation of fully substituted pyrazoles involve 1,3-dipolar cycloaddition of diazoalkanes or nitrile imines with olefins,²¹ the Knorr condensation of hydrazine with 1,3-dicarbonyl or their derivatives,²² the cross-coupling of 5-bromopyrazole derivatives with various nucleophiles or the sequential Suzuki coupling of pyrazole boronate derivatives using a metal directing group,²³ and by *N*-arylation of functionalized pyrazoles.²⁴ A one-pot synthesis of pyrazoles using Yb(PFO)₃ is also described under conventional conditions.²⁵ All above methods provided synthetic chemists with a multiple of choices to construct the substituted pyrazoles. Almost all of these methods suffer from one of the other drawbacks such as regiochemical infidelity, multistep sequence, low product yield, or longer reaction time, which has limited the exploitation of these methods in high throughput synthesis. Thus, an improved, efficient, and green alternative approach to functionalized pyrazoles is of current interest to synthetic chemists.

In continuation of our work on the development of facile and environmentally benign synthetic routes for the biologically important scaffolds²⁶ and fine chemicals²⁷, herein we wish to report our research on the combined catalytic system for the synthesis of highly substituted pyrazoles. We found that the equimolar mixture of Niobium pentachloride and Silver perchlorate (NbCl₅-AgClO₄) worked as an environmentally friendly, heterogeneous catalytic system for efficient synthesis of substituted pyrazoles (**4**) from one pot, multi-component reaction between phenyl hydrazine (**1**), ethylacetoacetate (**2**) and variety of aldehydes (**3**), at room temperature. (Scheme-1)

Scheme-1: Synthesis of Substituted Pyrazoles Catalyzed by NbCl₅-AgClO₄

EXPERIMENTAL

All the chemicals used were purchased from the Loba or Merck chemical companies and used without further purification. ¹HNMR and ¹³CNMR spectra were recorded on Bruker Avance-II FT-NMR (400 MHz). The MASS spectra were run on the Waters micro mass Q-ToF Micro mass spectrometer. The IR spectra were recorded on Perkin Elmer RX-I FTIR spectrometer. The melting points were carried in open capillary tubes by gradual heating in paraffin oil. The chemical structures were drawn using Chem. Draw. 0.8 version of Cambridge software.

General Procedure

First, a mixture of phenyl hydrazine (2 mmol), ethyl acetoacetate (2 mmol) and NbCl₅-AgClO₄ (5 mol %) was stirred magnetically at room temperature in dichloromethane (10 ml) for the formation of intermediate pyrazole as indicated by TLC, followed by the addition of aromatic aldehyde (1 mmol) in the same reaction vessel, the resulting reaction mixture was stirred maintaining identical conditions for the time specified in Table-1. The progress of the reaction was monitored by the TLC using n-hexane and ethyl acetate as the mobile phase. After the completion of the reaction, the reaction mixture was filtered to separate the catalyst and the solvent was removed under reduced pressure. So obtained crude product was washed with an aqueous brine solution, dried in oven and purified by recrystallization or column

chromatography as per the need. The structures of the synthesized products were confirmed from their physical and analytical data such as melting range, ^1H NMR, ^{13}C NMR, and Mass spectra.

Spectroscopic Data of Representative Compounds

4,4'-(Phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (4a)

^1H NMR (DMSO- d_6 , 400 MHz) δ : 2.33 (s, 6H), 4.97 (s, 1H), 7.16-7.21 (m, 1H), 7.23 7.31 (m, 6H), 7.45 (t, 4H), 7.72 (d, 4H), 12.44 (br. s, 1H, OH), 13.96 (br. s, 1H, OH); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 11.5, 33.1, 120.5, 125.5, 125.8, 127.1, 128.1, 128.8, 142.1, 146.2 ppm; Elem. Anal. Calc. for $\text{C}_{27}\text{H}_{24}\text{N}_4\text{O}_2$: C (74.29%), H (5.54%), N (12.84%). Found: C (74.28%), H (5.53%), N (12.82%).

4,4'-(p-Tolylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (4b)

^1H NMR (DMSO- d_6 , 400 MHz) δ : 2.25 (s, 3H), 2.32 (s, 6H), 4.91 (s, 1H), 7.08 (d, 2H, $J = 8.0$ Hz), 7.15 (d, 2H), 7.25 (t, 2H), 7.44 (t, 4H), 7.72 (d, 4H), 12.41 (br s, 1H, OH), 13.93 (br s, 1H, OH); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 11.6, 20.4, 32.7, 120.4, 125.5, 127.0, 128.6, 128.8, 134.7, 139.1, 146.2; Elem. Anal. Calc. for $\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_2$: C (74.65%), H (5.82%), N (12.44%); Found: C (74.63%), H (5.81%), N (12.43%).

4,4'-(p-Methoxyphenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (4c)

^1H NMR (DMSO- d_6 , 400 MHz) δ : 2.46 (s, 6H), 3.85 (s, 3H), 5.05 (s, 1H), 6.99 (d, 2H, $J = 8.4$ Hz), 7.31(d, 2H, $J = 8.8$ Hz), 7.40 (t, 2H, $J = 7.2$ Hz), 7.59 (t, 4H, $J = 7.6$ Hz), 7.86 (d, 4H, $J = 8.0$ Hz), 13 12.54 (s, br, 1H, OH), 14.07 (s, br, 1H, OH) ppm; ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 11.5, 32.3, 54.9, 113.4, 120.4, 125.5, 128.1, 128.8, 134.0, 146.1, 157.4 ppm; Elem. Anal. Calc. for $\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_3$: C (72.09%), H (5.62%), N (12.01%), Found: C (72.08%), H (5.60%), N (12.00%).

4,4'-(p-Chlorophenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (4d)

^1H NMR (DMSO- d_6 , 400 MHz) δ : 2.32 (s, 6H), 4.97 (s, 1H), 7.26 (d, 4H, $J = 8.2$ Hz), 7.34 (d, 2H, $J = 8.0$ Hz), 7.44 (t, 4H, $J = 7.1$ Hz), 7.71 (d, 4H, $J = 7.6$ Hz), 12.43 (br, 1H, OH), 13.87 (br, 1H, OH) 13 ppm; ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 12.0, 33.0, 121.0, 126.1, 128.5, 129.4, 129.6, 131.0, 141.6, 146.7 ppm; Elem. Anal. Calc. for $\text{C}_{27}\text{H}_{23}\text{ClN}_4\text{O}_2$: C (68.86%), H (4.92%), N (11.90%); Found: C (68.85%), H (4.91%), N (11.88%).

4,4'-(p-Nitrophenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (4e)

^1H NMR (DMSO- d_6 , 400 MHz) δ : 2.35 (s, 6 H), 5.13 (s, 1 H), 7.25–7.27 (m, 2 H), 7.44 (t, 4 H), 7.52 (d, 2 H), 7.71 (d, 4 H), 8.17 (d, 2 H), 12.64 (br s, 1 H, OH) ppm, ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 34.0, 56.8, 121.4, 124.2, OH), 13.86 (br, 1 H, OH) ppm; 126.5, 129.4, 129.8, 146.7, 147.1, 151.2 ppm; Elem. Anal. Calc. for $\text{C}_{27}\text{H}_{23}\text{N}_5\text{O}_4$: C (67.35%), H (4.81%), N (14.54%); Found: C (67.34%), H (4.80%), N (14.52%).

4,4'-(p-Cyanophenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (4f)

^1H NMR (DMSO- d_6 , 400 MHz) δ : 2.34 (s, 6H), 5.08 (s, 1H), 7.25 (t, 2H, $J = 7.2$ Hz), 7.43 7.47 (m, 6H), 7.70 (d, 4H), 7.77 (d, 2H), 12.55 (br s, 1H, OH), 13.86 (br s, 1H, OH); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 11.5, 33.2, 108.7, 118.9, 120.5, 125.6, 128.3, 128.9, 132.0, 132.1, 146.3, 148.1 ppm; Elem. Anal. Calc. for $\text{C}_{28}\text{H}_{23}\text{N}_5\text{O}_2$: C (72.87%), H (5.02%), N (15.17%); Found: C (72.86%), H (5.01%), N (15.15%).

4,4'-(o-Hydroxyphenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (g)

^1H NMR (DMSO- d_6 , 400 MHz) δ : 2.30 (s, 6H), 5.18 (s, 1H), 6.70 6.76 (m, 2H), 6.96 7.0 (m, 2H), 7.24 (t, 2H), 7.44 (t, 4H), 7.57 (d, 1H), 7.71 (d, 4H), 12.40 13 (s, br, 1H, OH) ppm; ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 11.7, 27.2, 114.7, 118.5, 120.5, 125.4, 125.5, 126.8, 128.7, 128.8, 129.2, 146.2, 153.8 ppm; Elem. Anal. Calc. for $\text{C}_{27}\text{H}_{24}\text{N}_4\text{O}_3$: C (71.67%), H (5.35%), N (12.38%); Found: C (72.66%), H (5.35%), N (12.37%).

4,4'-(p-Hydroxyphenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (4h)

^1H NMR (DMSO- d_6 , 400 MHz) δ : 2.31 (s, 6H), 4.86 (s, 1H), 6.67 (d, 2H), 7.05 (d, 2H), 7.25 (t, 2H), 7.45 (t, 4H), 7.72 (d, 4H), 9.16 (s, 1H, OH), 13 12.35 (br s, 1H, OH), 13.93 (br s, 1H, OH) ppm; ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 11.6, 32.3, 114.8, 120.4, 125.4, 125.5, 128.0, 128.8, 132.2, 146.1, 155.4 ppm;

Elem. Anal. Calc. for $C_{27}H_{24}N_4O_3$: C (71.67%), H (5.35%), N (12.38%); Found: C (72.64%), H (5.34%), N (12.37%).

RESULTS AND DISCUSSION

The preliminary study was aimed to examine the catalytic behavior of singular $NbCl_5$, $AgClO_4$ and the equimolar mixture of Niobium pentachloride and Silver perchlorate ($NbCl_5$ - $AgClO_4$). For this study, a model reaction between phenyl hydrazine, ethylacetoacetate, and benzaldehyde was considered. Three separate model reactions with 10 mol % of, one using $NbCl_5$, other using $AgClO_4$ and third with $NbCl_5$ - $AgClO_4$ as the catalysts and one more blank model reaction (without catalyst) were studied under identical conditions. The results obtained were quite inspiring, the blank reaction didn't produce any considerable amount of final product even after the stirring of 24 hours. Among catalyzed reactions, the reaction with $NbCl_5$ - $AgClO_4$ completed much earlier than the other two reactions containing individual $NbCl_5$ and $AgClO_4$ catalysts. This study revealed that the combination of $NbCl_5$ and $AgClO_4$ has greater potential to catalyze the synthesis of bis (pyrazolyls) or fully substituted pyrazoles over the individual compounds.

In the next part of the study, the most suitable solvent for the transformation at room temperature was selected. For this study, various organic solvents viz. ethanol, dichloromethane, tetrahydrofuran, dimethylformamide, dioxane, dimethylsulphoxide and distilled water were employed to above model reaction under the stirring condition at room temperature; it was found that the reaction took the longest time in distilled water and the shortest time in dichloromethane, while it took intermediate times to complete in the rest of the solvents. With the selected catalyst and solvent system, the study has been moved forward to optimize the amount of catalyst for better yields in the shortest reaction time. The model reaction has studied with gradually increased amounts of catalysts from 1 mol % to 10 mol % by the interval of 1 mol %. It was observed that with the increase in the amount of catalyst from 1 mol % to 5 mol %, the yields varied proportionally while the reaction time varied inversely. Beyond the 5 mol % amount of catalyst, the reaction showed no considerable effect on reaction time and product yield. Hence 5 mol % of $NbCl_5$ - $AgClO_4$ was established as the amount of catalyst sufficient to produce optimum yields in the shortest reaction time under the stirring condition at room temperature.

To examine the generality of the optimized catalytic protocol various aromatic aldehydes having various substituents have been employed for the title transformation. It was observed that all the employed aldehydes underwent the reaction smoothly to offer good to excellent yields of the products in 1.5 to 4.0 hours of reaction times, the results are summarized in Table-1. Aromatic aldehyde bearing substituent at 2-position took longer reaction times as observed in case of salicylaldehyde, reflected the effect of steric crowding at the reaction center in terms of longer reaction times as well as poor yields (table-1, entry g), while the aldehydes with electron-withdrawing groups at 3 or 4-position showed short reaction times and good to excellent yields (Table-1, entry c and e).

Table-1: $NbCl_5$ - $AgClO_4$ Catalysed Synthesis of Fully Substituted Pyrazoles From Phenylhydrazine, Ethylacetoacetate and Aldehydes under Optimised Conditions.

Entry	Reactants			Product	Reaction Time (hrs)	Yield* (%)
	1	2	3			
a.				4a	2.0	88
b.				4b	1.5	85
c.				4c	1.5	87

d.				4d	3.0	86
e.				4e	2.5	78
f.				4f	3.5	74
g.				4g	3.5	76
h.				4h	4.0	65
i.				4i	2.5	79
j.				4j	1.5	82

^aIsolated yields.

The potential of $\text{NbCl}_5\text{-AgClO}_4$ to catalyze the present synthesis was compared with some of the recently reported catalysts viz. *L-proline*²⁸, $\text{Zn}(\text{L-proline})_2$ ²⁸, guanidinium chloride²⁹, CoCl_2 ³⁰ and Mn(II) ³¹. It was observed that the present protocol produces better yields in shorter reaction times than all these reported catalysts. This ascertained the superiority of the present protocol over the reported catalysts.

CONCLUSION

$\text{NbCl}_5\text{-AgClO}_4$ was observed as an efficient, heterogeneous catalyst for the one-pot synthesis of fully substituted pyrazole from the pseudo five-component reaction between aromatic aldehyde, phenyl hydrazine and ethyl acetoacetate at room temperature in dichloromethane solvent. The need for a small amount of catalyst, heterogeneous condition, easy work-up procedure, mild reaction conditions, and good yields are the key features of the protocol.

ACKNOWLEDGMENT

Authors' are thankful to the director, School of Chemical Sciences, S.R.T.Marathwada University, Nanded. Maharashtra, India.

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[RJC-5728/2020]