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RESEARCH ARTICLE

ONE POT THREE COMPONENT SYNTHESIS OF ARYLIDINE DERIVATIVES CATALYSED BY SODIUM PHOSPHATE

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ABSTRACT

A series of 4-arylidene-3-methyl-5-pyrazolone derivatives were synthesized by reaction of various substituted aromatic aldehydes with 3-methylpyrazolone through Knoevenagel condensation by conventional method. We synthesized benzylidine derivatives by using sodium phosphate as a catalyst to obtain high yield, less reaction time with higher purity.

INTRODUCTION

Pyrazolone are defined as oxo derivatives of five-membered heterocycle containing two adjacent nitrogen atoms. They contain two double bonds within the nucleus, imparting an aromatic character to these molecules. Pyrazolone chemistry began in 1883 when Ludwig Knorr first react phenyl hydrazine with acetoacetic ester. When pyrazolones were discovered as coupling components for azo dyes in the late 1800s, they rapidly increased in importance. Pyrazolone are still economically important precursors for dyes and pharmaceuticals today.

Pyrazolone is a biologically important scaffold associated with multiple pharmacological activities such as antimicrobial[1-5], anti-inflammatory[6], analgesic[7], antidepressant[8], anticonvulsant[9], antidiabetic[10], anti hyperlipidemic[11-12], antiviral[13-14], anti tubercular[15-16], antioxidant[17-18], anticancer[19-20] etc. The synthesis of pyrazolone and its derivatives have engrossed substantial attention from organic and medicinal chemists for many years as they belong to a class of compounds with proven utility in medicinal chemistry.

Compounds with a reactive methylene group, pyrazolones react at C-4 with aldehydes and ketone. Several workers have demonstrated that the Knoevenagel condensation of 3-methyl-1-phenyl-2-pyrazolin-5-one with aromatic aldehydes in the presence of a catalyst (ethylenediammonium diacetate (EDDA)[18], magnesium oxide (MgO)[19], lithium bromide[20], potassium fluoride[21], or triethylamine[22] resulted in the corresponding 4-benzylidene-3-methyl-1-phenyl-2-pyrazolin-5-ones. Also, this condensation can be efficiently performed under MW irradiation[23-24].

MATERIALS AND METHODS

General

All research chemicals were purchased from Sigma-Aldrich and S.D. Fine Chemicals India Pvt. Ltd. and used as such for the reactions. Reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel plates.

Melting points of the synthesized compounds were determined by open capillary method and are uncorrected. UV spectra were recorded on Shimadzu 1700 UV–Visible spectrophotometer and IR spectra were recorded on Shimadzu 8400S FTIR spectrometer using KBr pellets. The 1H NMR were recorded on Bruker WM-300 (at 300 MHz) using CDCl3 as solvent. Chemical shifts are reported in δ ppm units with respect to TMS as internal standard. Purity of the compounds was checked on precoated TLC plates using silica gel G plates and iodine vapors as visualizing agent.

Synthesis

General procedure for the synthesis of 4-benzylidene-3-methyl-1H-pyrazol-5(4H)-one

Pure ethyl acetoactate (0.02 mol) was mixed with pure hydrazine hydrate (0.02 mol), followed by addition substituted aromatic aldehyde (0.02 mol). The catalyst was used in 10 mol% solution in water. The reaction was carried out at room

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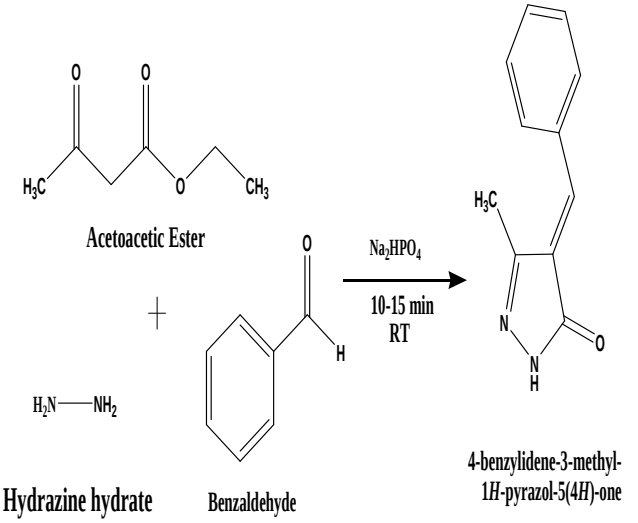
temperature. The reaction progressed was monitored by TLC. The product was obtained in 10-15 min, filters the product wash with water & recrystalized with ethanol solvent.



Scheme

Spectral Data

Synthesis of 4-benzylidene-3-methyl-1H-pyrazol-5(4H)-one

IR (KBr) cm^1:- 1524-1609, 1592, 1680, 3250, 3058.**^{1}HNMR (δ) ppm $CDCl_3$:-** 2.321 (s, 3H, CH3), 5.013 (s, H, CH), 7.413-7.956 (m, 5H), 7.1 (s, H, NH).**^{13}CNMR (δ) ppm:**-147.0, 143.4, 126, 135.4, 128.7, 128.0, 126.7, 126.4.

Synthesis of 3-methyl-4-(4-nitrobenzylidene)-1H-pyrazol-5(4H)-one

IR (KBr) cm^1:-, 1580, 1670, 3250, 3060, 1383, 1573, 1534-1610.**^{1}HNMR (δ) ppm $CDCl_3$:-** 2.21 (s, 3H, CH3), 5.13 (s, H, CH), 7.43-7.56 (m, 5H), 7.1 (s, H, NH).**^{13}CNMR (δ) ppm:-** 147.01, 143.6, 126, 135.7, 128.8, 128.1, 126.6, 126.3.

Synthesis of 3-methyl-4-(4-flurobenzylidene)-1H-pyrazol-5(4H)-one

IR (KBr) cm^1:-, 1591, 1688, 2922, 3060, 1315, 1560-1600.**^{1}HNMR (δ) ppm $CDCl_3$:-** 2.23 (s, 3H, CH3), 5.23 (s, H, CH), 7.43-7.65 (m, 5H), 7.2 (s, H, NH).**^{13}CNMR (δ) ppm:-** 144.01, 142.4, 126, 132.7, 126.8, 127.1, 126.6, 127.3.

Synthesis of 3-methyl-4-(4-chlorobenzylidene)-1H-pyrazol-5(4H)-one

IR (KBr) cm^1:-, 1588, 1678, 2930, 3120, 1315, 1504-1625.**^{1}HNMR (δ) ppm $CDCl_3$:-** 2.25 (s, 3H, CH3), 5.33 (s, H, CH), 7.52-7.74 (m, 5H), 7.34 (s, H, NH).**^{13}CNMR (δ) ppm:-** 143.0, 142.6, 128, 137.7, 128.8, 124.1, 126.6, 127.3.

Synthesis of 3-methyl-4-(4-Hydroxybenzylidene)-1H-pyrazol-5(4H)-one

IR (KBr) cm^1:- 1595, 1676, 2929, 2979, 3423. **^{1}HNMR (δ) ppm $CDCl_3$:-** 2.22 (s, 3H, CH3), 5.70 (s, H, CH), 7.40-7.54 (m, 5H), 7.51 (s, H, NH).**^{13}CNMR (δ) ppm:**-144.0, 145.01, 128, 135.7, 130.8, 125.1, 126.6, 127.3.

Synthesis of 3-methyl-4-(4-methoxybenzylidene)-1H-pyrazol-5(4H)-one

IR (KBr) cm^1:- 1545, 1655, 1109-1245, 3423. **^{1}HNMR (δ) ppm $CDCl_3$:-** 2.32 (s, 3H, CH3), 5.20 (s, H, CH), 7.52-7.61 (m, 5H), 7.51 (s, H, NH).**^{13}CNMR (δ) ppm:**-145.0, 147.01, 124, 139.7, 135.8, 128.1, 121.6, 124.3.

RESULT AND DISCUSSION

Synthetic method for the preparation of 4-arylidene-3-methyl-5-pyrazolone derivatives are summarized in above Scheme. It is clear from the scheme that the new heterocyclic compounds possess pyrazolone unit. Reaction of 3-methyl-5-pyrazolone with aromatic aldehydes proved to be a convenient route to fulfill this aim. Synthesis of 3-methyl-5-pyrazolone was carried out by reacting hydrazine hydrate with ethylacetoacetate with constant stirring. The reaction involved in final step is an example of the Knoevenagel condensation, in which the active methylene group at position-4 of 3-methyl-5-pyrazolone reacts with aromatic aldehydes to form 4-arylidene-3-methyl-5-pyrazolone derivatives. The reaction was carried out in the presence of sodium phosphate. The final compounds were obtained in good yields.

Table Physical data of synthesized compounds

Sr. No	Aldehyde	Melting point (°C)	Yield (%)
1	Benzaldehyde	88-92	75
2	4-Nitrobenzaldehyde	114-116	86
3	4-flurobenzaldehyde	98-102	82
4	4-chlorobenzaldehyde	81-83	68
5	4-hydroxybenzaldehyde	209-211	85
6	4-Methoxybenzaldehyde	104-105	60

CONCLUSION

In the present study, the synthesis, spectral studies of a novel series of 4-arylidene-3-methyl-5-pyrazolone derivatives are being reported. These heterocyclic compounds containing pyrazolone ring systems were prepared by the Knoevenagel condensation between 3-methyl-5-pyrazolone and aromatic aldehydes in sodium phosphate catalyst. The compounds were synthesized by conventional method also and the time for synthesis was reduced from hours to just a 10-15 minutes.

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