A FACILE SOLVENT FREE MICROWAVE INDUCED SYNTHESIS OF SOME SUBSTITUTED PYRAZOLINES

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ABSTRACT-

A novel one pot acetylation of substituted pyrazolines were prepared from 7-(substitutedbezylidiene)-3-(substituted phenyl)-3,3a,4,5,6,-pentahydrocyclo-hexa(c)-2H-Pyrazoline (IVa-d) and 6-(substituted bezylidiene)-3-(substituted phenyl)-3,3a,4,5,-tetrahydrocyclo-penta(c)-2H-pyrazoline (IVe–IVh) (0.01M), has been carried out using microwave irradiation with the solvent free reaction afforded title compounds in 80-90% yield with high purity.

KEYWORDS :- N- Acetylation, Pyrazoline, Microwave irradiation .

INTRODUCTION

Pyrazoline and their derivatives are known to possess impressive biological activities. They have been reported to have bactericidal[1.2,] acaridal [3,4 ,] anti-inflammatory [5-], antidepressant[6], anipyretic[7], antibacterial[8] and antifungal [9] properties. Recently reported studies on the microwave irradiation for the synthesis of heterocyclic compounds revealed that it is safe, rapid, economic and convenient, eco friendly method for chemical synthesis. Pollution free synthesis, lesser reaction time, easy work up, and minimum use of solvent are the major advantages of this technique[10-12]

EXPERIMENTAL ,MATERIAL AND METHODS-: All chemicals used were of analytical grade. All the synthesized compounds have been characterized on the basis of chemical properties, elemental and spectral analysis. The melting points were measured in a open glass capillary and are uncorrected .IR spectra in KBr were recorded on instrument Perkin Elmer - Spectrum RX-IFTIR. 1 H-NMR spectra were recorded on FT NMR Spectrometer model Advance-II (Bruker) Its 1 H frequency is 400 MHz 13C the frequency is 100 MHz ($CDCl_3$ and DMSO-d6) using TMS as an internal standard All reactions were monitored by TLC using silica gel 60-f-254plates. All reactions were carried out in scientific microwave oven (Scientific microwave system model RG31lL1, 700w, 2450MHz).satisfactory C, H, N analysis were carried out for most of the compounds on Thermo Scientific (FLASH 2000) CHN Elemental Analyzer at RSIC, Punjab University, Chandigarh

General Procedure For Synthesis of -(substituted benzylidiene)-3-(substituted phenyl)-3.3a.4,5,6 pentahydrocyclohex (c) pyrazol-(2-yl)-ethanone(VIa-d) and 6-(substituted benzylidiene)-3-(substituted phenyl)- 3,3a,4,5,-tetrahydrocyclopenta(c) pyrazol-2-yl)ethanone (VI e-h)

N-acetyl substituted pyrazolines were prepared from 7-(substitutedbezylidiene)-3-(substituted phenyl)-3,3a,4,5,6,-pentahydrocyclo-hexa(c)-2H-Pyrazoline (IVa-d) and 6-(substituted bezylidiene)-3-(substituted phenyl)-3,3a,4,5,-tetrahydrocyclo-penta(c)-2H-pyrazoline (IVe–IVh) (0.01M), acetic anhydride and sodium acetate in acetic acid. The reaction is carried out in microwave for 5 to 6 min at 700W. The reaction mixture was cooled to room temperature and extracted with ethyl acetate. After concentration under reduced pressure it was left at room temperature. The solid separated was filtered dried and recrystallized to afford sample of (VIa-VIh).

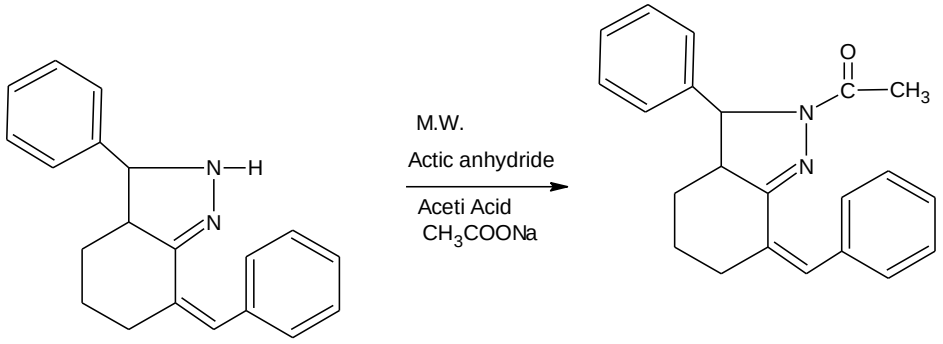


Table 1: Physical data of some 7-(substituted benzylidiene)-3-(substituted phenyl)-3.3a.4,5,6 pentahydrocyclohex (c) pyrazol-(2-yl)-ethanone(VIa-d) and 6-(substituted benzylidiene)-3-(substituted phenyl)- 3,3a,4,5,-tetrahydrocyclopenta(c) pyrazol-2-yl)ethanone (VI e-h)

Compound	R	Molecular formula	M.P. ^{0}C	Reaction Time (min.)	Yield (%)
7-benzylidiene-3-phenyl-3.3a.4,5,6pentahydrocyclohexa(c)pyrazol-(2-yl)-ethanone.(VIa)	C_6H_5	$C_{22}H_{22}N_2O$	131	5	87
7-(4-chlorbenzylidiene)-3-(4-chlorophenyl)-3.3a.4,5,6pentahydrocyclohexa(c)pyrazol-(2-yl)-ethanone.(VIb)	C_6H_5Cl	$C_{22}H_{20}Cl_2N_2O$	165	6	89
7-(4-bromobenzylidiene)-3-(4-bromophenyl)-3.3a.4,5,6pentahydrocyclohexa(c)pyrazol-(2-yl)-ethanone.(VIc)	C_6H_5Br	$C_{22}H_{20}Br_2N_2O$	132	6	78
7-(2,4 dichlorobenzylidiene)-3-(2,4 dichlorophenyl)-3.3a.4,5,6pentahydrocyclohexa(c)pyrazol-(2-yl)-ethanone.(VId)	$C_6H_4Cl_2$	$C_{22}H_{18}Cl_4N_2O$	167	5	85
6- benzylidiene-3- phenyl-3,3a,4,5,-tetrahydrocyclopenta(C) pyrazol-2-yl)ethanone(VIe)	C_6H_5	$C_{21}H_{20}N_2O$	120	6	89
6-(4-chlorobenzylidiene)-3-(4-chlorophenyl)- 3,3a,4,5,-tetrahydrocyclopenta(C) pyrazol-2-yl)ethanone(VIf)	C_6H_5Cl	$C_{21}H_{18}Cl_2N_2O$	132	5	74
6-(4-bromobenzylidiene)-3-(4-bromophenyl)- 3,3a,4,5,-tetrahydrocyclopenta(C) pyrazol-2-yl)ethanone(VIg)	C_6H_5Br	$C_{21}H_{18}Br_2N_2O$	130	6	84
6-(2,4dicholrobenzylidiene)-3-(2,4 dicholrophenyl)-3,3a,4,5,-tetrahydrocyclopenta(C)pyrazol-2-yl)ethanone(VIh)	$C_6H_4Cl_2$	$C_{21}H_{16}Cl_4N_2O$	134	6	80

ANALYTICAL DISCUSSION

1)Synthesis of 7-benzylidiene-3-phenyl-3.3a.4,5,6pentahydrocyclohexa(c)pyrazol-(2-yl)-ethanone(VIa)-The compound (VIa) is a whitish crystalline solid.,M. P..131^{0}C ,The analytical results indicated the molecular formula of the compound (**VIa**) as $C_{22}H_{22}N_2O$ The I.R. spectrum of compound (VIa) showed the following main absorption bands.3168(s) C-H Steching, 2924(m) C-Hstrech(aliphatic), 1896(m) Combination band(monosubstituted),1731(s) C=O,1641(s) C=N, 1641,1582,1563(s) C=C,1401**(s)** CH_2bend,1463(s)CH_3 asymmetricalbending,1379(s) CH_3 symmetricalbending,1307(s)
C-N

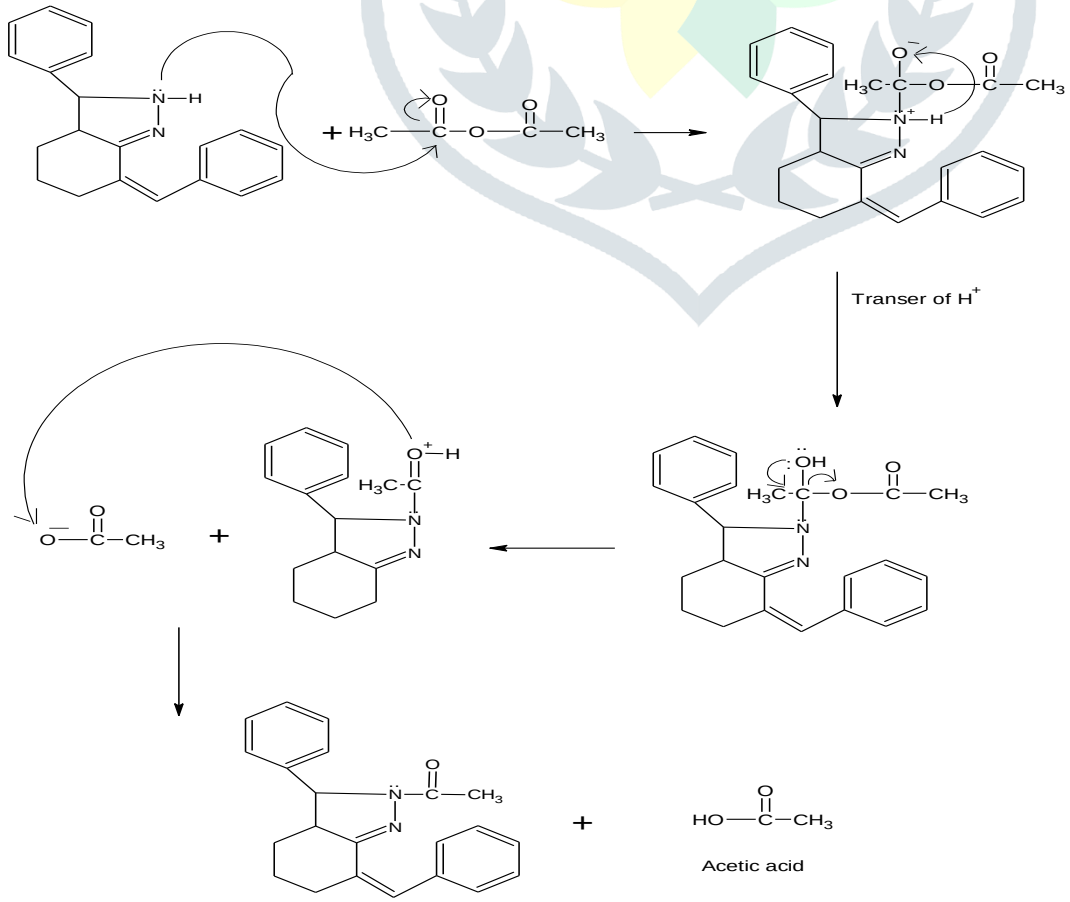
The PMR spectrum of compound (VIa) was reported in (DMSO-d6) wth TMS as an internal standard- 0.8-0.9 (m) 2H,CH_2 , 1.6-1.7(dd) 1H(-CH) ,1.2 -1.37(m),4H ,2(CH_2) ,2.17 (s) 3H, $COCH_3$, 2.53(t) 1H (-CH),4.14(m) 1H(=CH) , 7.4 -8.2(m) 10H[Ar-H(^{3}J =6.8)]

2) Spectral data for confirmation of (4-bromobenzylidiene)-3-(4-bromophenyl)-3.3a.4,5,6pentahydrocyclohexa(c)pyrazol-(2-yl)-ethanone.(VIc) - IR (KBr.Cm -1-)-)- 2885 (C-H Stret.), 1664,1660 (CHO), 1430, 2350 (C=C and C=N). **^{1}H** – NMR(DMSO)- 1.4-1.2(DD, 1H,C-Ha),3,83-3.93 (dd, 1H, C-Hb), 4.9(methane) , 6.90-7.39(m,9H,Ar-H),7.01(s,1-BR) , 10.12 (s,1H,CHO) **,^{13}C-NMR(**DMSO)-26.4 (CH_2),33.6(cyclohexaneCH_2) , 135(imine), 134.1(benzen)

3) Spectral data for confirmation of Synthesis of 7-(2,4 dichlorobenzylidiene)-3(2,4dichlorophenyl)3.3a.4,5,6-pentahydrocyclohexa (c) pyrazol-(2-yl)-ethanone (VId)- The compound (VId) is yellowish crystalline solid, The IR spectrum of the compound (VId) showed the following absorption bands 3088 (s) C-H stretch(aromatic), 2923(m) C-H stretch(aliphatic), 1919(m) Combination band(1,2,4 trisubstituted, 1731(s) C=O ,1615(s) C=O, 1615,1582,1545(s) C=C , 1487(s) CH_3 asymmetrical bending,1467(s) CH_2bend , 1383(s) CH_3 symmetrical bending, 1317(s) C-N ,1101(s) C-Cl, 865(s) 1,2,4 trisubstituted oop,

The PMR spectrum of compound ((VId) was recorded – 0.82-0.92(m) 2H, CH_2 ,1.2 -1.4(m)2H, CH_2,1.6-1.7(m) 2H CH_2, 2.5(s) 3H, COCH3 , 2.7-3.0 (s) 1H,-CH ,2.8(dd)1H,-CH ,4.15(m) 1H, =CH ,7.4-8.1(m) 6H, Ar-H.

PROBABLE MECHANISM -



Result

In above synthetic scheme we use microwave irradiation technique, this is a solvent free reaction condition that leads to considerable saving in the reaction time and energetically profitable. The solvent free condition contributes to saving in cost and diminishes the waste disposal problem.

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