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SYNTHESIS OF SUBSTITUTED NITRO-CHALCONES AND 3, 5-DIARYL-NITRO-Δ^2-PYRAZOLINES

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ABSTRACT

Five different chalcones **(Ia)** to **(If)** were synthesized by condensing 2-hydroxy-3-nitro-5-methyl acetophenone with six different aromatic aldehydes in ethanol using NaOH. These chalcones were cyclized with 2, 4-dintrophenylhydrazine in ethanol yielding **(IIa)** to **(IIf)**. The synthesized compounds were characterized by IR and NMR spectral analysis.

Key words: Nitrochalcones, Pyrazolines.

INTRODUCTION

Chalcones are synthesized by condensation of 2-hydroxyacetophenone with aromatic aldehydes in presence of acidic[1] or basic[2] media. Chalcones show amoebicidal and antimicrobial activities[3]. Since pyrazolines have antibacterial, antifungal and insecticidal activity[4-7], these are effective in killing houseflies on contact[8]. Pyrazolines have microbial activity also[9]. Some workers studied biological evalution of some novel pyrazolines[10]. Pyrazolines show antimicrobial activity in quinoline based-2-pyrazolines[11].

EXPERIMENTAL

Melting points of all synthesized compounds were determined in open capillary tube and are uncorrected. The purity of compounds were checked by TLC using silica G. I. R. spectra were recorded on Perkin-Elmer-841 spectrometer (cm^{-1}) in KBr disc and NMR (Brucker 300 MHz) using DMSO as solvent.

Synthesis of 2-hydroxy-3-nitro-5-methyl-acetophenone (I)

p-Cresyl acetate was prepared from p-cresol by known method. Then by Fries

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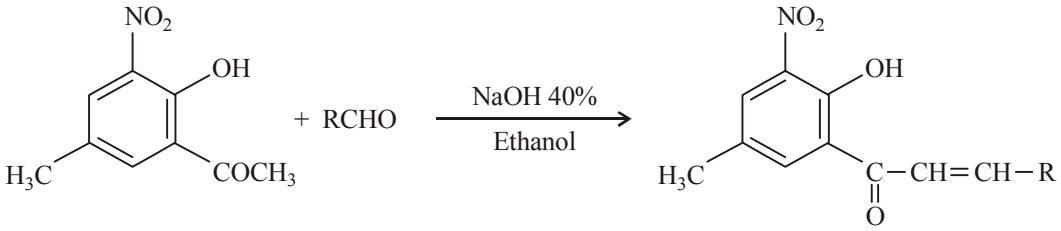
migration, 2-hydroxy-5-methyl acetophenone was obtained, which on nitration gives 2-hydroxy-3-nitro-5-methyl acetophenone.

Synthesis of substituted 2-hydroxy-3-nitro-5-methyl chalcones (Ia – If)

Compounds **(Ia–If)** were synthesized from 2-hydroxy-3-nitro-5-methyl acetophenone by reacting it with six different aromatic aldehydes by reported method in solvent ethanol using 40% NaOH. The physical data of compound **(Ia)** to **(If)** are given in Table 1.

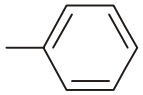
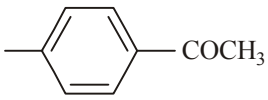
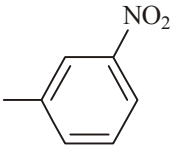
Reaction Scheme 1



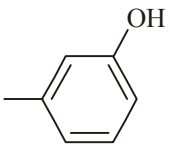
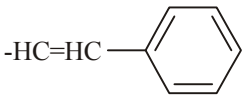
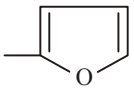
(I) **(Ia - If)**

The groups R are shown in Table 1.

Table 1

Compound No.	R	Mol. formula	M.P. (^{0}C)	Yield (%)
(Ia)		$C_{16}H_{13}NO_4$	120	66
(Ib)		$C_{17}H_{15}NO_5$	117	68
(Ic)		$C_{16}H_{12}N_2O_6$	118	62

Cont...

Compound No.	R	Mol. formula	M.P. (^{0}C)	Yield (%)
(Id)		$C_{16}H_{13}NO_5$	140	70
(Ie)		$C_{18}H_{15}NO_4$	152	63
(If)		$C_{14}H_{11}NO_5$	92	60

Characterization data of compound (Ia)

IR (KBr) cm^{-1}: 3066.91 (hydrogen bonded OH stretching), 1641.48 (C=O stretching), 1558.54 (C-CH=CH stretching), 1348.29 (Ar-O stretching) and 1170.83 (stretching in phenol).

NMR data: 2.3 δ [(s) 3H, Ar-CH_3), 6.9 δ (dd, 1H = CH_a)], 7.1 δ [(dd, 1H = CH_b), 7.2 – 8.1 δ (m, 7H Ar-H)] and 9.95 δ [s, 1H – OH phenolic)]

Characterization data of compound (Id)

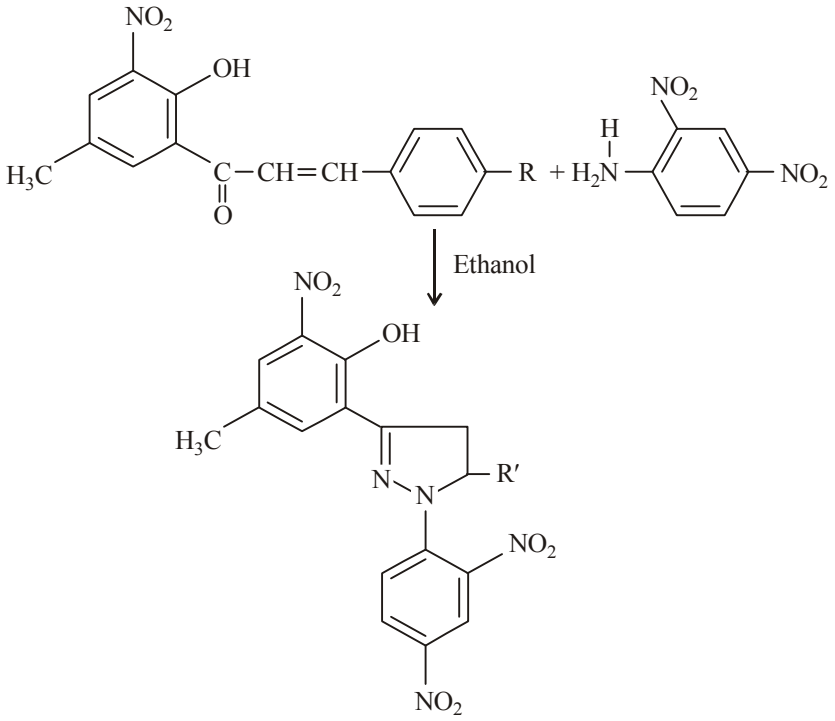
IR (KBr) cm^{-1}: 3578.07 (S, 1H – phenolic (OH), 3500.92 (S, 1H, phenolic OH), 1637.62 (C = O stretching), 1556.61 (C – CH = CH stretching), 1529.60 & 1350.22 (NO_2 stretching), 1247.99 (phenolic – OH stretching, Ar-O stretching) and 1159.26 (stretching in phenol).

NMR data: 2.25 – 2.30 δ (S, 3H, Ar – CH_3), 6.9 δ (1H = CHa), 7.1 δ (1H, C = CHb), 7.7 – 8.4 (m, 6H, Ar – H), 10.25 δ (Ar – OH), 13.3 δ (Ar – OH)

Synthesis of substituted -3,5-diaryl-nitro-Δ^2- pyrazolines (IIa – IIf)

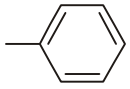
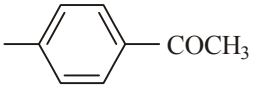
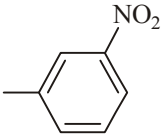
Nitrochalcones **(Ia – If)** (0.01M) and 2, 4-dinitrophenylhydrazine (0.02M) were refluxed in 20 mL ethanol for 3.5 to 4.5 hours. Further processing was same as done in an earlier method. Thus, compounds **(IIa – IIf)** were synthesized and recrystallized. Physical data are shown in Table 2.

Reaction Scheme 2

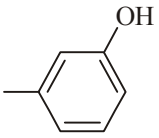
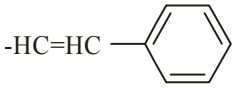
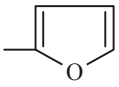


The groups R′ are given in Table 2.

Table 2

Compound No.	R'	Mol. formula	M.P. (^{0}C)	Yield (%)
(IIa)		$C_{22}H_{17}N_5O_7$	164	68
(IIb)		$C_{23}H_{19}N_5O_7$	145	72
(IIc)		$C_{22}H_{16}N_6O_9$	118	62

Cont...

Compound No.	R'	Mole. Formula	M.P. (^{0}C)	Yield (%)
(IId)		$C_{22}H_{17}N_5O_8$	160	66
(IIe)		$C_{24}H_{19}N_5O_7$	105	60
(IIf)		$C_{20}H_{15}N_5O_8$	180	61

Characterization data for compound (IIa)

IR (KBr) in cm^{-1}: 3325.39 (br, OH stretching in Ar – OH), 1643 (S, CH_2 stretching), 1606.76 (C = N stretching), 1417.73 (CH_2 in pyrazoline), 1269.20 (C – N stretching) and 1062.81 (C – O stretching).

NMR data: 2.3 – 2.35 δ (s, 3H, Ar – CH_3), 3.2 δ (dd, 1H, dd > CHH_a) 3,3 δ (dd, 1H, > CHH_b), 5 – 5.2 δ (1H, CH_x), 7 – 8.5 δ (m, 10H, Ar – H) and 10 δ (Ar – OH)

Characterization data for compound (IId)

IR (KBr) cm^{-1}: 3471.80 – 3458.48 (br, Ar–OH), 3325.39 (br Ar–OH), 1614.47 (S, CH_2 streching), 1591.33 (C = N streching), 1417.73 (CH_2 – streching in pyrazoline), 1512.24 and 1332.86 (NO_2 streching), 1224 (C – N streching) and 1134.18 (C – O streching in phenol).

NMR data: 2.15 – 2.35 δ (s, 3H, Ar – CH_3), 3.25 δ (dd, 1H, CHH_a), 3.3 δ (dd, 1H, CHH_b), 5.1 δ (1H, CH_x), 7.1 – 7.6 δ (m, 9H – Ar – H), 9 δ (s, 1H, Ar – OH) and 10 δ (s, 1H Ar – OH).

RESULTS AND DISCUSSION

Compound **(Ia – If)** and **(IIa – IIf)** were synthesized through the route as shown in reaction schemes. Physical data of compounds are shown in Tables 1 and 2. The structures of synthesized compounds **(Ia)**, **(Id)**, **(IIa)** and **(IId)** were confirmed on the basis of IR and NMR elemental analysis.

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