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Synthesis of 1,1-bis-{2-Hydroxy-3-[1′-Phenyl/H-5′-Aryl-Pyrazolin-3′-yl]-5-Methyl Phenyl} Methanes

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Some new 1,1-bis-{2-hydroxy-3-[1′-phenyl/H-5′-aryl-pyrazolin-3′-yl]-5-methyl phenyl} methanes (**7a—h** and **8a–h**) have been synthesized by the action of 1,1-bis-{2-hydroxy-3-(3-aryl-prop-2-en-1-one)-5-methyl phenyl} methanes (**5a–h**) with phenyl hydrazine hydrochloride and hydrazine hydrate in pyridine medium.

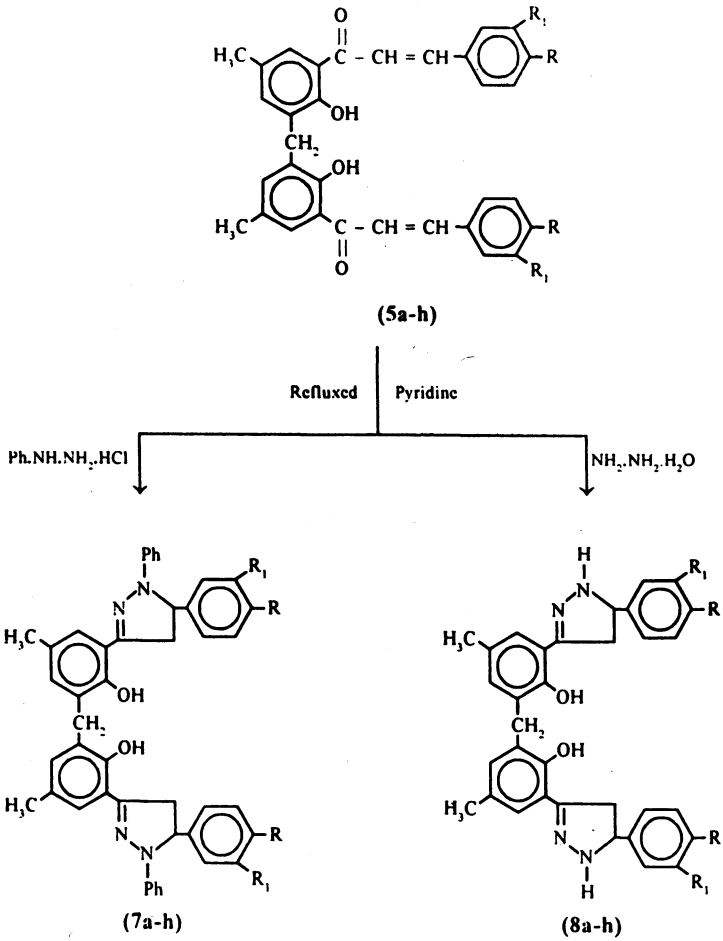
Key Words: Synthesis, Bis-pyrazolines, 1,1-Bis-{2-hydroxy-3-[1′-phenyl/H-5′-aryl-pyrazolin-3′-yl]-5-methyl phenyl} methanes.

INTRODUCTION

Pyrazolines are the dihydrate form of pyrazoles and are well known five-membered nitrogen containing heterocyclic compounds. Various procedures have been developed for their synthesis. Formation of pyrazolines has been reported[1, 2] by the action of nucleophile like hydrazine hydrate or phenyl hydrazine etc. on flavanones and chalcones in solvents like acetic acid, pyridine, alcohol, etc. Pyrazolines have been found to be luminescent and fluorescent agents.[3, 4] They are also used in textiles and killing house flies[5], antipyretics[6], anti-inflammatory[7], antifungicidal[8], analgesic[9] and antimicrobial properties.[10, 11] Some pyrazolines show electro-luminescence property.[12] Also 3,3′-bis-(1′-H) and (1-acetyl) pyrazolines[13] and 1,1-bis-(1′-benzoyl) and (1′-pyridoyl) pyrazolines have been reported.[14]

1,1-Bis-{2-hydroxy-3-[1′-phenyl/H-5′-aryl-pyrazolin-3′-yl]-5-methyl phenyl} methanes are not yet synthesized. It was therefore thought of interest to synthesize bis-pyrazolines.

The present work deals with the synthesis of 1,1-bis-{2-hydroxy-3-[1′-phenyl-5′-aryl-pyazolin-3′-yl]-5-methyl phenyl} methanes **(7a–h)** and 1,1-bis-{2-hydoxy-3-[1′-H-5′ayl-pyrazolin-3′-yl]-5-methyl phenyl} methanes **(8a-h)** by action of nucleophile phenyl hydrazine hydrochloride and hydrazine hydrate with 1,1-bis-{2-hydroxy-3-(3′-aryl-prop-2-en-1-one)-5-methyl phenyl} methanes **(5a–h).** The structures of these compounds are established on the basis of elemental analysis and spectral analysis (UV, IR and NMR etc.).



Scheme

EXPERIMENTAL

All melting points were taken in a silicon oil bath instrument in an open capillary and are uncorrected. Purity of compounds was checked by TLC on silica gel-G. IR-spectra were recorded on a Perkin-Elmer-577 spectrophotometer, PMR spectra on a Bruker AC 300 FNMR spectrometer (300 MHz) and UV spectra on a Shimadzu UV-160 spectrophotometer. Nitrogen was estimated on Colman-29-N analyzer.

Preparation of 1,1-bis-{2-hydroxy-3-[1′-phenyl-5′-aryl-pyrazolin-3′-yl]-5-methyl phenyl} methanes (7a–h)

1,1-Bis-{2-hydroxy-3-[1′-phenyl-5′-aryl-pyrazolin-3′-yl]-5-methyl phenyl} methanes **(7a–h)** were synthesized by refluxing 1,1-bis-{2-hydroxy-3-(3′-aryl-

prop-2-en-1-one)-5-methyl phenyl} methane (**5a–h**) (0.01 M) with phenyl hydrazine hydrochloride (0.04 M) in solvent pyridine for 5–6 h. Then reaction mixture was decomposed by water containing acid (HCl). The obtained product was filtered and washed with $NaHCO_3$ (2%) followed by water and crystallized from acetic acid.

Preparation of 1,1-bis-{2-hydroxy-3-[1′-H-5′-aryl-pyrazolin-3′-yl]-5-methyl phenyl} methanes (8a–h)

1,1-Bis-{2-hydroxy-3-[1′-H-5′-aryl-pyrazolin-3′-yl]-5-methyl phenyl methanes (**8a–h**) were synthesized by refluxing 1,1-bis-{2-hydroxy-3-(3′-aryl-prop-2-en-1-one)-5-methyl phenyl} methanes (**5a–h**) (0.01 M) with hydrazine hydrate (0.04 M) in solvent pyridine for 5–6 h. The reaction mixture was decomposed by water containing HCl. The obtained product was filtered and washed with $NaHCO_3$ (2%) followed by water and crystallized from acetic acid.

The physical and analytical data of (**7a–h**) and (**8a–h**) are given in Table-1.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF 1,1-BIS-{2-HYDROXY-3-[1′-PHENYL/H-5′-ARYL-PYRAZOLIN-3′-YL]-5-METHYL PHENYL} METHANES

Compds.	R	R′	m.p. (°C)	Yield (%)	m.f.	N% Found	N% (Calcd.)
7a	H	H	288–231	75	$C_{45}H_{40}N_4O_2$	8.16	8.38
7b	OCH_3	H	218–222	74	$C_{47}H_{44}N_4O_4$	7.53	7.69
7c	OH	OCH_3	265–267	72	$C_{47}H_{44}N_4O_6$	7.12	7.36
7d	OH	H	268	78	$C_{45}H_{40}N_4O_4$	9.62	8.00
7e	NO_2	H	278	80	$C_{45}H_{38}N_6O_6$	12.47	11.08
7f	$N(CH_3)_2$	H	201	85	$C_{49}H_{50}N_6O_2$	10.35	11.14
7g	H	OCH_3	198–201	70	$C_{47}H_{44}N_4O_4$	7.27	7.69
7h	OCH_3	OCH_3	235–238	72	$C_{49}H_{48}N_4O_6$	7.03	7.10
8a	H	H	250–253	78	$C_{33}H_{32}N_4O_2$	9.67	10.85
8b	OCH_3	H	246–249	76	$C_{35}H_{36}N_4O_4$	9.61	9.72
8c	OH	OCH_3	221–224	82	$C_{35}H_{36}N_4O_6$	9.07	9.21
8d	OH	H	255–258	75	$C_{33}H_{32}N_4O_4$	11.33	10.21
8e	NO_2	H	273	80	$C_{33}H_{30}N_6O_6$	14.22	13.86
8f	$N(CH_3)_2$	H	173–176	82	$C_{37}H_{42}N_6O_2$	13.22	13.95
8g	H	OCH_3	186–189	68	$C_{35}H_{36}N_4O_4$	9.32	9.72
8h	OCH_3	OCH_3	213–215	70	$C_{37}H_{40}N_4O_6$	8.07	8.80

Spectral Interpretation of (7a)

IR (ν_{max}) (cm^{-1}): 3398 ν(—OH); 2921 ν(C—H); 1609 ν(C=N); 1461 ν(C=C); 1253 ν(C—O).

NMR ($CDCl_3$) δ ppm: 2.41 (s, 6H, $—CH_3$); 3.31 (dd, 2H, $—CHH_A$); 3.64 (dd, 2H, $—CH_BH$); 4.25 (s, 2H, Ar—CH_2—Ar); 4.95 (dd, 2H, $—CH_x$); 6.76–7.53 (m, 24H, Ar—H); 11.45 (s, 2H, Ar—OH).

UV(λ_{max}): 363 nm.

Spectral Interpretation of (8a)

IR (ν_{max}) (cm^{-1}): 3367 ν(—OH); 3311 ν(N—H); 2915 ν(C—H); 1600 ν(C=N); 1495 ν(C=C); 1250 ν(C—O).

NMR ($CDCl_3$) δ ppm: 2.26 (S, 6H, $—CH_3$); 3.19 (dd, 2H, $—CHH_A$); 3.83 (dd, 2H, $—CH_BH$); 4.11 (s, 2H, Ar—CH_2—Ar); 5.10 (dd, 2H, $—CH_x$); 6.63–7.93 (m, 24H, Ar—H); 10.96 (s, 2H, —NH); 13.06 (s, 2H, Ar—OH).

UV(λ_{max}): 348 nm.

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