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NOTE

Synthesis of 3-Substituted Phenyl-4-Arylidene-5-[(2′-O-Carbamyl) 5′/6′-Methyl Phenyl] Pyrazoles

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The synthesis of some new 3-substituted phenyl-4-arylidine-5-[(2′-o-carbamyl) 5′/6′-methyl phenyl] pyrazoles have been reported. The strategy employed for the synthesis involved the reaction of 2′-hydroxy, 5′/6′-methyl-2-benzoyl-3-aryl-acrylophenones with hydrazine hydrate to give targeted pyrazoles II_{a-m}. The structures of these compounds have been confirmed by elemental analysis and ir, nmr spectral studies.

Pyrazoles form a very important class of heterocyclic compounds which do not occur in nature. Many pyrazole derivatives are known to possess wide ranging activities[1-4]. They also act as good antiviral agents[5-7], analgesics[8], depressants[9], antiinflammatory[10-13] and antidiabetic[14] agents. Recently, some 3-phenyl-4-arylidine-5-o-hydroxyphenyl-pyrazoles have been reported[15]. Here, we report the synthesis of some new pyrazoles derived from substituted acrylophenones.

The preparation of substituted o-hydroxy dibenzoyl methanes II_{a-m} were carried out by Baker Venkatraman[16] transformation of o-aryloxy-acetophenones under catalysed conditions followed by base catalysed condensation with various aromatic aldehydes to form acrylophenones II_{a-m}. The compounds II_{a-m} when reacted with phenyl isocyanate in THF in the presence of triethylamine yielded corresponding urethanes III_{a-m} in a quantitative yield. Urethanes of 2′-hydroxy-5′/6′-methyl-2-benzoyl-3-phenyl acrylophenones when condensed with hydrazine hydrate in acetic acid gave title compounds IV_{a-m} respectively (Scheme 1).

All the melting points were determined by open capillary method and are not corrected. IR-spectra were recorded in KBr pellets on Perkin-Elmer spectrophotometer. PMR-spectra (TFA) were run on Perkin Elmer 90 MHZ spectrometer using TMS as internal standard. The purity of the compounds in addition to elemental analysis was checked by TLC.

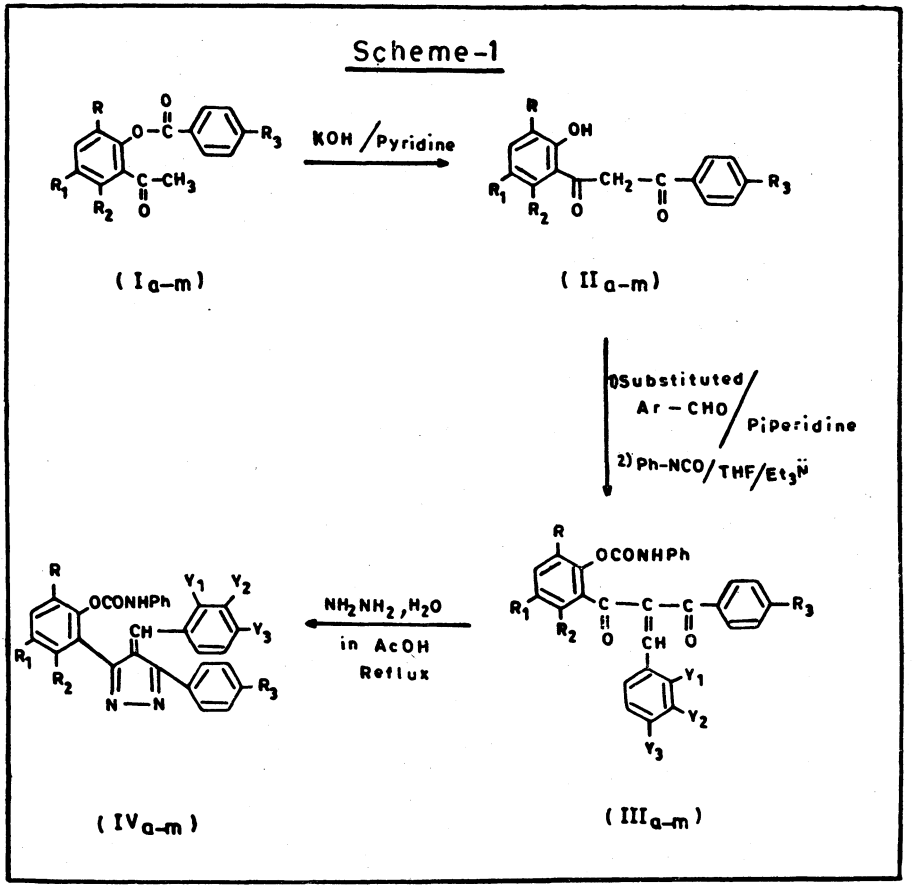
The o-hydroxy-5-methyl dibenzoyl methanes I_{a-m}, 2′-hydroxy, 5′/6′-methyl-2-benzoyl-3-aryl acrylophenones[17] II_{a-m} and substituted 2′-o-carbamyl, 5′/6′-methyl-2-benzoyl-3-aryl acrylophenones[18] III_{a-m} were prepared by known method.

The following procedure forms a general method for the preparation of corresponding pyrazoles IV_{a-m}.

TABLE 1

PHYSICAL DATA OF 3-SUBSTITUTED PHENYL-4-ARYLIDENE-5-(2′-o-CARBAMYL, 5′/6′-METHYL PHENYL) PYRAZOLES

Compd. No.	R	R_1	R_2	R_3	Y_1	Y_2	Y_3	Molecular formula	M.P. (°C)	Analysis of N % Found/(Calculated)
IV_b	H	$-CH_3$	H	$-NO_2$	H	H	—OCONHPh	$C_{37}H_{26}N_4O_{10}$	130	8.00 (8.16)
IV_c	H	H	$-CH_3$	$-NO_2$	$-OCH_3$	H	$-OCH_3$	$C_{32}H_{26}N_4O_6$	215	10.50 (10.56)
IV_d	$-NO_2$	$-CH_3$	H	$-NO_2$	$-OCH_3$	H	$-OCH_3$	$C_{31}H_{25}N_9O_8$	194	11.75 (11.89)
IV_e	H	$-CH_3$	H	H	H	H	—OCONHPh	$C_{37}H_{27}N_4O_4$	175	9.40 (9.49)
IV_f	$-NO_2$	$-CH_3$	H	$-NO_2$	H	H	$-N(CH_3)_2$	$C_{02}H_{26}N_6O_6$	225	14.20 (14.22)
IV_g	$-NO_2$	$-CH_3$	H	—Cl	H	H	$-N(CH_3)_2$	$C_{32}H_{26}N_5O_4Cl$	188	12.00 (12.08)
IV_h	$-NO_2$	H	H	$-NO_2$	H	H	$-OCH_3$	$C_{30}H_{21}N_5O_7$	140	12.35 (12.44)
IV_i	$-NO_2$	$-CH_3$	H	$-NO_2$	H	H	$-NO_2$	$C_{30}H_{20}N_6O_8$	155	14.10 (14.19)
IV_j	H	$-CH_3$	H	$-NO_2$	H	—Cl	H	$C_{30}H_{21}N_4O_4Cl$	180	10.40 (10.43)
IV_k	H	$-CH_3$	H	$-NO_2$	H	H	$-N(CH_3)_2$	$C_{32}H_{27}N_5O_4$	110	12.80 (12.84)
IV_l	H	H	$-CH_3$	$-NO_2$	H	H	—OCONHPh	$C_{37}H_{27}N_5O_6$	185	10.75 (10.81)
IV_m	H	H	$-CH_3$	$-NO_2$	H	H	$-N(CH_3)_2$	$C_{32}H_{27}N_5O_5$	202	12.50 (12.61)



3-substituted phenyl-4-arylidine-5-(2'-o-carbamyl, 5'/6'-methyl phenyl) pyrazoles (IV_a): A mixture of 2'-hydroxy, 5'/6'-methyl-2-benzoyl-3-arylacrylophenones (0.552 g, 0.001 mole) and hydrazine hydrate (3.5 ml, 20%) in 5 ml. of glacial acetic acid was refluxed for about 1½ hr., cooled and poured into ice cold water. The separated solid was filtered and recrystallized from ethanol to furnish IV_a (0.4 g., 71.5 %). M.P. 155°C (found: C, 69.80; H, 5.15; N, 8.35. $C_{32}H_{26}O_4N_3Cl$ calcd. for: C, 69.88, H, 5.2; N, 8.4 %). IR (KBr): ν_{max} (cm^{-1}) 3300–3250 (—NH); 1720 (—O—CO), 1620 (—C=N), 1600 (—C=C); 1150 (C—O—C); NMR (TFA): δ(PPM), 2.3 (3H, s, Ar—CH_3), 3.83 (3H, s, —OCH_3); 7 – 7.5 (10 H, M., aromatic protons), 8.4 (1H, s, CONH exchangeable with D_2O).

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