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Reaction of pyridinium phenacylids and their picolinium and isoquinolinium counterparts with substituted benzylideneacetophenones gave a wide variety of 2,4,6-triaryl-substituted pyridines which are expected to have some potential biological activities. Ammonium acetate in glacial acetic acid was used as the cyclization agent. The structures of resulting pyridines are supported by nmr and ir spectral data.

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Although considerable work has been done by various workers (1,2) in order to examine the reactivity of pyridinium ylids towards benzylideneacetophenones, the synthetic potentialities of picolinium and isoquinolinium ylids have been comparatively less explored after the only report of Krohnke, *et al.*, (3). Continuing our previous researches, (4-7), presently we wish to report the synthesis of some new 2,4,6-triaryl-substituted pyridines *via* pyridinium, picolinium and isoquinolinium ylids generated *in situ* from their respective precursors.

Pyridinium phenacylids, 4-picolinium phenacylids and isoquinolinium phenacylids were generated *in situ* from their respective cycloimmonium salts (1-3) and were made to react with wide range of substituted benzylideneacetophenones (4a-s) in refluxing acetic acid in presence of ammonium acetate to afford a wide variety of 2,4,6-triaryl-substituted pyridines (6a-s) presumably *via* the intermediacy of pentane-1,5-dionylpyridinium, 4-picolinium and isoquinolinium derivatives (5a-s), respectively (Scheme 1).

All the pyridines synthesized in this study are listed in Table 1. The products (6a-s), most of which are new, gave satisfactory elemental analysis. The structures of the final products were supported by nmr and ir spectral data (Table 2).

EXPERIMENTAL

Melting points were measured on Gallen kamp apparatus and are uncorrected. The ir spectra were recorded on Perkin-Elmer infracord spectrophotometer in potassium bromide. The nmr spectra (deuteriochloroform) were determined using a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Analytical samples were purified by column chromatography over neutral alumina and purity was checked by thin layer chromatography (tlc).

Pyridinium, 4-picolinium and isoquinolinium salts (1-3) were prepared by the quaternization of tertiary bases *viz.*, pyridine, 4-picoline and isoquinoline with the respective α -bromoketones.

Preparation of 2,4,6-Triaryl-substituted Pyridines (6a-s).

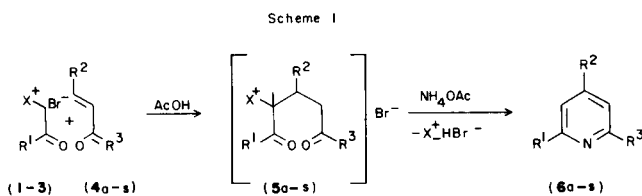
A general procedure was used in all the reactions. A mixture of *N*-acylcycloimmonium salts (1-3, 3 mmoles) and ammonium acetate (3 g.) in acetic acid (15 ml.) was stirred at 80°. Benzylideneacetophenones (4a-s, 3 mmoles) in 10 ml. of acetic acid was added dropwise during 1 hour after which the temperature was allowed to raise up to 120°. Heating was continued for additional 3 hours. The mixture was left overnight at room temperature and ice cold water was then added to precipitate a solid which was separated, washed with methanol, dried and crystallized from an appropriate solvent to yield 2,4,6-triaryl-substituted pyridines (6a-s).

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1a = X = C₅H₅N

1b = X = "

1c = X = "

1d = X = "

2a = X = 4-CH₃-C₅H₄N

2b = X = 4-CH₃-C₅H₇N

3a = X = C₉H₇N

3b = X = C₉H₇N

R¹ = 4-OCH₃-C₆H₄

R¹ = 4-CH₃-C₆H₄

R¹ = 4-Cl-C₆H₄

R¹ = 4-C₆H₅-C₆H₄

R¹ = 4-Cl-C₆H₄

R¹ = 4-CH₃-C₆H₄

R¹ = 4-CH₃-C₆H₄

R¹ = 3-NO₂-C₆H₄

Table 1
Structure and Physical Properties of 2,4,6-Triarylsubstituted Pyridines

Compound	R ¹	R ²	R ³	Salt used	% Yield	M.p. °C	Crystallization solvent (a)	Analysis Found (Calcd.) %		
								C	H	N
6a	4-OCH ₃ -C ₆ H ₄	3,4-(OCH ₃) ₂ -C ₆ H ₃	3-NO ₂ -C ₆ H ₄	1a	60	146-147	A	70.60 (70.58)	5.00 (4.97)	6.31 (6.33)
6b	4-CH ₃ -C ₆ H ₄	4-OCH ₃ -C ₆ H ₄	4-CH ₃ -C ₆ H ₄	1b	55	140-141	A	85.50 (85.48)	6.28 (6.30)	3.84 (3.83)
6c	4-CH ₃ -C ₆ H ₄	4-OCH ₃ -C ₆ H ₄	4-OCH ₃ -C ₆ H ₄	1b	45	116-117	A	82.72 (82.76)	6.12 (6.10)	3.72 (3.71)
6d	4-CH ₃ -C ₆ H ₄	3,4-(OCH ₃) ₂ -C ₆ H ₃	C ₆ H ₅	1b	55	97-99	A	82.73 (82.76)	6.08 (6.10)	3.73 (3.71)
6e	4-CH ₃ -C ₆ H ₄	4-N(CH ₃) ₂ -C ₆ H ₄	4-Cl-C ₆ H ₄	1b	62	138-139	A	78.76 (78.79)	5.74 (5.77)	7.00 (7.02)
6f	4-CH ₃ -C ₆ H ₄	4-Cl-C ₆ H ₄	4-OCH ₃ -C ₆ H ₄	1b	58	145-146	A	77.80 (77.82)	5.16 (5.19)	3.65 (3.63)
6g	4-CH ₃ -C ₆ H ₄	4-N(CH ₃) ₂ -C ₆ H ₄	4-OCH ₃ -C ₆ H ₄	1b	52	122-123	A	82.21 (82.23)	6.58 (6.60)	7.11 (7.10)
6h	4-CH ₃ -C ₆ H ₄	C ₆ H ₅	4-OCH ₃ -C ₆ H ₄	1b	48	101-102	B	85.43 (85.47)	5.96 (5.98)	3.98 (3.99)
				3b	56	100-101	B	85.42 (85.47)	5.96 (5.98)	3.96 (3.99)
6i	4-Cl-C ₆ H ₄	4-OCH ₃ -C ₆ H ₄	4-OCH ₃ -C ₆ H ₄	1c	45	123-125	A	74.68 (74.71)	4.97 (4.98)	3.48 (3.49)
6j	4-Cl-C ₆ H ₄	4-N(CH ₃) ₂ -C ₆ H ₃	4-Cl-C ₆ H ₄	1c	48	155-156	A	71.58 (71.60)	4.79 (4.77)	6.69 (6.68)
6k	4-Cl-C ₆ H ₄	3,4-(OCH ₃) ₂ -C ₆ H ₃	4-Cl-C ₆ H ₄	1c	50	169-170	A	68.78 (68.80)	4.38 (4.36)	3.20 (3.21)
				2a	52	168-170	A	68.76 (68.80)	4.37 (4.36)	3.21 (3.21)
6l	4-C ₆ H ₅ -C ₆ H ₄	3,4-(OCH ₃) ₂ -C ₆ H ₃	4-CH ₃ -C ₆ H ₄	1d	50	69-70	A	84.04 (84.02)	5.84 (5.90)	3.09 (3.06)
6m	4-C ₆ H ₅ -C ₆ H ₄	4-OCH ₃ -C ₆ H ₄	4-CH ₃ -C ₆ H ₄	1d	54	147-148	A	87.28 (87.32)	5.61 (5.63)	3.26 (3.28)
6n	4-CH ₃ -C ₆ H ₄	3,4-(OCH ₃) ₂ -C ₆ H ₃	4-Cl-C ₆ H ₄	1b	50	130-131	A	75.08 (75.09)	5.28 (5.29)	3.37 (3.36)
				2b	55	132-133	A	75.08 (75.09)	5.30 (5.29)	3.38 (3.36)
6o	4-Cl-C ₆ H ₄	3,4-(OCH ₃) ₂ -C ₆ H ₃	C ₆ H ₅	2a	58	59-60	B	74.68 (74.71)	4.97 (4.98)	3.48 (3.49)
6p	4-CH ₃ -C ₆ H ₄	3,4-(OCH ₃) ₂ -C ₆ H ₃	C ₆ H ₅	2b	52	112-113	A	81.22 (81.25)	6.75 (6.77)	3.62 (3.64)
				3a	50	116-117	A	81.24 (81.25)	6.78 (6.77)	3.63 (3.64)
6q	4-CH ₃ -C ₆ H ₄	4-CH ₃ -C ₆ H ₄	4-CH ₃ -C ₆ H ₄	3a	62	176-177	A	89.41 (89.39)	6.61 (6.59)	4.04 (4.01)
6r	4-CH ₃ -C ₆ H ₄	C ₆ H ₅	4-CH ₃ -C ₆ H ₄	3a	58	145-146	A	89.52 (89.55)	6.22 (6.26)	4.21 (4.18)
6s	3-NO ₂ -C ₆ H ₄	4-OCH ₃ -C ₆ H ₄	4-Cl-C ₆ H ₄	3b	60	181-183	A	69.13 (69.15)	4.10 (4.08)	6.69 (6.72)

(a) Solvent for crystallization. A = Pyridine-methanol. B = Chloroform-methanol.

Table 2
Nmr and Ir Data for 2,4,6-Triarylsubstituted Pyridines (6a-s)

Compound	Nmr data (deuteriochloroform)			Ir data (potassium bromide), cm ⁻¹		
	δ (ppm)	No of protons	Assignment	C-H stretching vibrations	C=C Vibration	C=N Vibration
6a	4.02 d	9H	methoxy	—	—	—
	6.94-8.44 m	13H	aromatic	—	—	—
6b	2.62 s	6H	methyl	—	—	—
	3.98 s	3H	methoxy	—	—	—
6c	6.94-8.60 m	14H	aromatic	—	—	—
	—	—	—	3010	1601	1550, 1500
6d	2.36 s	3H	methyl	—	—	—
	3.82 d	6H	methoxy	—	—	—
6e	6.84-8.15 m	14H	aromatic	—	—	—
	2.62 s	9H	methyl	—	—	—
6f	6.80-8.32 m	14H	aromatic	—	—	—
	2.42 s	3H	methyl	—	—	—
6g	3.88 s	3H	methoxy	—	—	—
	6.98-8.32	14H	aromatic	—	—	—
6h	2.76 s	9H	methyl	—	—	—
	3.82 s	3H	methoxy	—	—	—
6i	6.72-8.36 m	14H	aromatic	—	—	—
	2.42 s	3H	methyl	—	—	—
6j	3.82 s	3H	methoxy	—	—	—
	6.90-8.38 m	15H	aromatic	—	—	—
6k	—	—	—	3010	1600	1510, 1490
	—	—	—	3060	1600	1530, 1490
6l	—	—	—	—	1601	1520, 1495
	—	—	—	3060	1599	1535, 1508
6m	—	—	—	3040	1600	1542, 1510
	—	—	—	3020	1600	1510, 1490
6n	3.28 d	6H	methoxy	—	—	—
	5.74-6.82 m	14H	aromatic	—	—	—
6o	2.34 s	3H	methyl	—	—	—
	3.76 d	6H	methoxy	—	—	—
6p	6.63-8.11 m	14H	aromatic	—	—	—
	2.42 s	9H	methyl	—	—	—
6q	7.16-8.54 m	14H	aromatic	—	—	—
	2.40 s	6H	methyl	—	—	—
6r	7.08-8.56 m	15H	aromatic	—	—	—
	3.90 s	3H	methoxy	—	—	—
6s	6.98-8.60 m	14H	aromatic	—	—	—

s = singlet; d = doublet; m = multiplet.