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Synthesis of Some New 2,4,6-Triarylsubstituted Pyridines via Pyridinium Ylides

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Some new 2,4,6-triarylsubstituted pyridines, which are expected to possess marked biological activities were synthesized via 4-methylphenacylpyridinium ylide and 4-chlorophenacylpyridinium ylide. Ammonium acetate in acetic acid was used as the cyclization agent. The structures of the products were confirmed either by NMR or by IR spectrum analysis.

Pyridinium ylides, being versatile intermediates react with a wide variety of electrophilic substrates leading to the synthesis of cyclic and heterocyclic systems¹⁻⁴. Noteworthy in this respect are phenacylidene pyridinium ylides which because of their two reactive centres undergo interesting cyclization reactions¹⁻⁴.

Following our previous researches, on the reactivity of pyridinium ylides⁵⁻⁹, the present communication described the synthesis of some new 2,4,6-triarylsubstituted pyridines with a view to exploring the synthetic potentialities of this reaction.

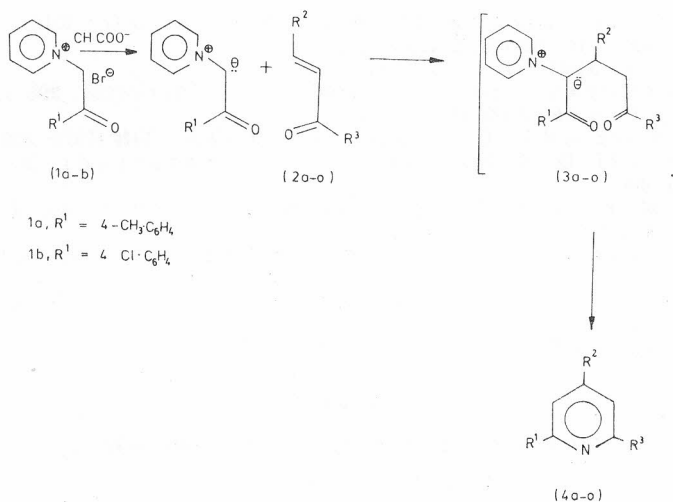
4-methylphenacylpyridinium bromide (**1a**) and 4-chlorophenacylpyridinium bromide (**1b**) were obtained in good yields as a result of quaternization of pyridine with the respective *N*-phenacyl bromides. The reaction of **1a—b** with various substituted benzylidene acetophenones in acetic acid using ammonium acetate as the cyclization agent yielded some new 2,4,6-triarylsubstituted pyridines (**4a—o**) (Scheme 1). The reaction presumably proceeds via an ylide carbanion intermediate which is generated from pyridinium salt (**1a—b**) and undergoes Michael type of addition on α , β -unsaturated carbonyl systems to yield the 1,5-dionylpyridinium derivative (**3a—b**) which on further reaction with ammonium acetate gives various 2,4,6-triarylsubstituted pyridines. All the pyridines synthesized are listed in Table I. The structures of the resulting pyridines are supported either by NMR or by IR spectrum analysis.

The infrared spectrum of the pyridines along with other absorption bands showed a characteristic absorption band in the region 3030—3000 cm^{-1} which is diagnostic of the CH stretching mode of the pyridine ring. The strong bands in the region 1600—1500 cm^{-1} have been assigned to the interaction between C=C and C=N vibrations of the pyridine ring. The former band appeared as double absorption maxima near 1600 cm^{-1} which appears to be a general

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TABLE I
Physical Properties of 2,4,6-Triarylsubstituted Pyridines (4a—0)

Compound	R ¹	R ²	R ³	Yield	M. p. °C	Recrystn. Solvent	Analysis found (Calcd)		
							C/%	H/%	N/%
4a	4-CH ₃ ·C ₆ H ₄	3,4(OCH ₃) ₂ ·C ₆ H ₃	4-CH ₃ ·C ₆ H ₄	60	112	Py/MeOH/H ₂ O	81.98 (82.02)	6.36 (6.32)	3.52 (3.54)
b	4-CH ₃ ·C ₆ H ₄	4-OCH ₃ ·C ₆ H ₄	4-Cl·C ₆ H ₄	45	151	Py/MeOH	77.86 (77.82)	5.20 (5.18)	3.65 (3.63)
c	4-CH ₃ ·C ₆ H ₄	C ₆ H ₅	-CH=CH·C ₆ H ₅	80	112	Py/MeOH/ Ethyl acetate	89.89 (89.91)	6.07 (6.05)	4.00 (4.03)
d	4-CH ₃ ·C ₆ H ₄	3-NO ₂ ·C ₆ H ₄	2-Naphthyl	75	121	Py/MeOH/H ₂ O	80.44 (80.38)	5.21 (5.26)	6.71 (6.69)
e	4-CH ₃ ·C ₆ H ₄	3,4(OCH ₃) ₂ ·C ₆ H ₃	2-thienyl	65	75	Py/MeOH/H ₂ O	74.38 (74.41)	5.45 (5.42)	3.63 (3.61)
f	4-CH ₃ ·C ₆ H ₄	C ₆ H ₅	2-thienyl	70	78—80	Py/MeOH/H ₂ O	80.69 (80.73)	5.22 (5.19)	4.31 (4.28)
g	4-CH ₃ ·C ₆ H ₄	4-OCH ₃ ·C ₆ H ₄	9-Anthryl	85	110	Py/MeOH	87.38 (87.41)	5.92 (5.96)	3.13 (3.09)
h	4-CH ₃ ·C ₆ H ₄	3,4-CH ₂ O ₂ ·C ₆ H ₃	4-C ₆ H ₅ ·C ₆ H ₄	90	137—8	Py/MeOH	83.96 (83.97)	5.59 (5.64)	3.19 (3.16)
i	4-CH ₃ ·C ₆ H ₄	4-OCH ₃ ·C ₆ H ₄	3-NO ₂ ·C ₆ H ₄	52	136	Py/MeOH/H ₂ O	75.80 (75.75)	5.01 (5.05)	7.09 (7.07)
j	4-CH ₃ ·C ₆ H ₄	3,4(OCH ₃) ₂ ·C ₆ H ₃	3-NO ₂ ·C ₆ H ₄	45	112	Py/MeOH/H ₂ O	76.11 (76.09)	5.35 (5.36)	6.79 (6.82)



characteristic of trisubstitution at the pyridine nucleus¹⁰⁻¹¹. The bands due to ring vibrations and CH deformations are observed near 1245 and 1020 cm^{-1} .

The nuclear magnetic resonance spectra of the products in general exhibited aromatic protons in the region δ 7.00—8.70. Peaks verifying the presence of methyl, methoxy and methylenedioxy groups appear in the range of δ 2.5—3.0; δ 3.8—4.0 and δ 6.00 respectively.

EXPERIMENTAL

Melting points were measured on a Gallenkamp apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer Infracord spectrophotometer in potassium bromide. The NMR spectra ($CDCl_3$) were run using a Varian A-60 spectrometer using tetramethylsilane as the internal standard. Analytical samples were purified by column chromatography over neutral alumina. Purity was checked by thin layer chromatography (TLC).

Pyridinium salts were prepared by treatment of α -bromoketones and pyridine in benzene at reflux temperature.

Preparation of 2,4,6-Triarylsubstituted Pyridines (4a—o)

A general procedure was used in all the reactions. To a stirred solution of 3 mmol of the pyridinium salts (**1a, b**) in 10 ml of glacial acetic acid in presence of ammonium acetate was added gradually a solution of α,β -unsaturated ketone (**3a—o**; 3 mmol) in 10.0 ml of glacial acetic acid under an inert atmosphere of nitrogen. The reaction mixture was stirred at reflux temperature for six hours and was kept at room temperature overnight. Then 30.0 ml of ice cold water was added and the precipitated product was washed twice with methanol and was recrystallised from the appropriate solvent mentioned in Table I.

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SAŽETAK

Sinteza novih 2,4,6-triaril supstituiranih piridina

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Sintetizirano je nekoliko novih 2,4,6-triaril supstituiranih piridina, koristeći 4-metilfenacilpiridinium ilid ili 4-klorfenacilpiridinium ilid kao intermedijere, a u prisutnosti amonijevog acetata u octenoj kiselini kao ciklizirajućeg agensa. Strukture produkata potvrđene su podacima iz NMR ili iz infracrvenih spektara.

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