Table II. *N*-Aryl-*N'*-(triorganostannyl)-*N'*,*N''*-dicyanoguanidines (RNHC(NCN)N(CN)SnR'$_3$)[a]

no.	R	R'	mp,[b] °C	IR spectra[c]			C_6H_5 ring vibration (*6–8*)	SnC_6H_5 (*8, 9–13*)	
				NH	C≡N	C=N		ν_{as}	ν_s
VI	C_6H_5	C_6H_5	185–187	3401 m	2165 s	1563 s	451 s	277 s[d]	230 s
VII	2-naphthyl	C_6H_5	210–212	3390 m	2203 s, 2155 s	1563 s	452 s[e]	276 s[f]	226 s
VIII	*p*-FC_6H_4	C_6H_5	163–165	3378 m	2165 s	1563 s	451 s[g]	277 s[h]	232 s
IX	*p*-$C_2H_5OC_6H_4$	C_6H_5	195–196	3367 w, 3205 w	2160 s	1563 s	452 s	275 s[i]	227 s
X	*p*-$O_2NC_6H_4$	C_6H_5	210–212	3390 m	2165 s	1570 s	451 s[j]	267 s[k]	231 s
XI[l]	C_6H_5	CH_3	180–182	3245 w, 3268 m	2212 s, 2169 s	1563 s			
XII[m]	2-naphthyl	CH_3	186.5–187.5	3289 w, 3413 w	2212 s, 2169 s	1590 s			

[a] Elemental analyses (C, H, N, F, and Sn) in agreement with theoretical values were obtained and submitted for review. [b] Refers to the analytical sample; recrystallization solvents were ethyl acetate (VI–VIII), acetonitrile (X–XII), and benzene (IX). [c] Values are expressed in cm^{-1}; s = strong, m = medium, w = weak. [d] Bands were present at 375 w and 342 cm^{-1}. [e] A band was present at 476 m cm^{-1}. [f] A band was present at 340 w cm^{-1}. [g] A band was present at 482 m cm^{-1}. [h] Bands were present at 377 w, 361 m, and 316 w cm^{-1}. [i] A band was present at 376 cm^{-1}. [j] A band was present at 490 w cm^{-1}. [k] Bands were present at 180 s, 202 m, 330 s, and 377 s cm^{-1}. [l] Bands were present at 551 s [ν_{as}(SnC)], 617 m, 500 m [(ν_s(SnC)], 380 w, 352 s, 284 s, and 208 m cm^{-1}. [m] Bands were present at 550 s [ν_{as}(SnC)], 597 w, 513 w, 499 w [ν_s(SnC)], and 468 s cm^{-1}.

and filtered to give 8.64 g (24%) of pure *N*-phenyl-*N'*-diethyl-*N''*-cyanoguanidine (II, Table I), mp 123–125 °C. The ethanol was evaporated from the filtrate, the residue was stirred with ethyl acetate, and the mixture was filtered to give 8.08 g (27%) of additional II, mp 123–125 °C (total yield of II, 51%).

Reaction of Bis(triphenylstannyl)carbodiimide with Ethyl N-(p-Ethoxyphenyl)thiocarbamate. A mixture of bis(triphenylstannyl)carbodiimide (14.80 g, 0.02 mol), ethyl *N*-(*p*-ethoxyphenyl)thiocarbamate (4.51 g, 0.02 mol), and acetonitrile (250 mL) was refluxed for 17 h. The acetonitrile was evaporated from the filtrate, the residue was stirred with carbon tetrachloride (200 mL), and the mixture was filtered to give 3.78 g of material, mp 138–140 °C. This material was stirred with hot ethanol, and the mixture was filtered to give 1.77 g (31%) of *N*-(*p*-ethoxyphenyl)-*N'*-(triphenylstannyl)-*N'*,*N''*-dicyanoguanidine (IX, Table II), mp 193–195 °C. A single recrystallization from benzene raised the melting point to 195–196 °C.

The carbon tetrachloride was evaporated from the original filtrate, the residue was stirred with hot ethanol (75 mL), and the mixture was cooled and filtered to give 10.69 g of bis(triphenyltin) sulfide, mp 140–141 °C.

Preparation of N-Phenyl-N'-(trimethylstannyl)-N',N''-dicyanoguanidine (XI, Table II). A mixture of bis(trimethylstannyl)carbodiimide (7.35 g, 0.02 mol), ethyl *N*-phenylthiocarbamate (3.63 g, 0.02 mol), and acetonitrile (250 mL) was refluxed for 15 h. The mixture was allowed to cool to 25 °C and then was filtered. The solvent was evaporated from the filtrate, the residue was stirred with carbon tetrachloride (250 mL), and the mixture was filtered to give 2.88 g of material, mp 145–150 °C. Recrystallization of this material from acetonitrile afforded 1.46 g (42%) of crude *N*-phenyl-*N'*-(trimethylstannyl)-*N'*,*N''*-dicyanoguanidine, mp 168–170 °C. A second recrystallization from acetonitrile gave 1.15 g (33%) of pure product, mp 180–182 °C.

Preparation of N-(2-Naphthyl)-N'-(trimethylstannyl)-N',N''-dicyanoguanidine (XII, Table II). A mixture of bis(trimethylstannyl)carbodiimide (7.35 g, 0.02 mol), ethyl *N*-(2-naphthyl)thiocarbamate (4.63 g, 0.02 mol), and acetonitrile (250 mL) was refluxed for 15 h. The acetonitrile was evaporated, the residue was stirred with carbon tetrachloride (250 mL) for 2 h, and the mixture was filtered to give 4.11 g of material, mp 130–145 °C. Recrystallization of this material from ethyl acetate/diethyl ether afforded 0.183 g (5%) of pure *N*-(2-naphthyl)-*N'*-(trimethylstannyl)-*N'*,*N''*-dicyanoguanidine, mp 184.5–185.5 °C. Recrystallization from acetonitrile gave the analytical sample, mp 186.5–187.5 °C.

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Studies on Cycloimmonium Ylides. Synthesis of Some 2,4,6-Triaryl-Substituted Pyridines via Picolinium Ylides

Ram. S. Tewari,* Ajay K. Dubey, Naresh K. Misra, and Priya D. Dixit

Department of Chemistry, H. B. Technological Institute, Kanpur-208002, India

A wide variety of 2,4,6-triaryl-substituted pyridines have been synthesized by the interaction of aroylmethylenepicolinium ylides with different α,β-unsaturated ketones. The structural assignments were based on microanalytical and spectral data.

Introduction

Extensive studies have been carried out in the reactions of pyridinium ylides and isoquinolinium ylides with α,β-unsaturated ketones following the first reports of Krohnke et al.[1-9] Almost no work has been done on picolinium ylides, and we therefore

Table I. Structure and Physical Properties of 2,4,6-Triaryl-Substituted Pyridines (Compounds 4a–u)[a]

compd	molecular formula	R^1	R^2	R^3	mp, °C obsd	mp, °C lit.	% yield	recrystallization solvent
4a	$C_{23}H_{17}N$	C_6H_5	C_6H_5	C_6H_5	138–139	137–138[b]	60	C_5H_5N–MeOH
4b	$C_{23}H_{15}Cl_2N$	C_6H_5	4-ClC_6H_4	4-ClC_6H_4	136–137	138–140[c]	60	C_5H_5N–MeOH
4c	$C_{30}H_{21}NO_2$	C_6H_5	3,4-$CH_2O_2C_6H_3$	4-biphenyl	156–158	155–156[c]	60	$CHCl_3$–MeOH
4d	$C_{29}H_{21}N$	C_6H_5	C_6H_5	4-biphenyl	135–136	138–139[d]	55	C_5H_5N–MeOH
4e	$C_{26}H_{23}NO_2$	C_6H_5	3,4-$(OCH_3)_2C_6H_3$	4-$CH_3C_6H_4$	116–118	120–121[c]	60	C_5H_5N–MeOH
4f	$C_{25}H_{18}ClN$	4-ClC_6H_4	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	179–181	183–184[c]	55	$CHCl_3$–MeOH
4g	$C_{24}H_{15}ClNO_2$	4-ClC_6H_4	3,4-$CH_2O_2C_6H_3$	4-ClC_6H_4	186–188	188–189[c]	60	$CHCl_3$–MeOH
4h	$C_{24}H_{17}Cl_2NO$	4-ClC_6H_4	4-$OCH_3C_6H_4$	4-ClC_6H_4	183–184	180–181[c]	60	$CHCl_3$–MeOH
4i	$C_{25}H_{20}ClNO_2$	4-ClC_6H_4	3,4-$(OCH_3)_2C_6H_3$	C_6H_5	100–101	100–101[c]	50	C_5H_5N–MeOH
4j	$C_{26}H_{22}ClNO_2$	4-ClC_6H_4	3,4-$(OCH_3)_2C_6H_3$	4-$CH_3C_6H_4$	134–136	140–141[c]	50	C_5H_5N–MeOH
4k	$C_{25}H_{21}NO$	4-$CH_3C_6H_4$	C_6H_5	4-$OCH_3C_6H_4$	98–100		50	C_5H_5N–MeOH
4l	$C_{26}H_{23}N$	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	170–172		60	$CHCl_3$–MeOH
4m	$C_{26}H_{23}NO_2$	4-$CH_3C_6H_4$	4-$OCH_3C_6H_4$	4-$OCH_3C_6H_4$	120–122		50	C_5H_5N–MeOH
4n	$C_{26}H_{23}NO_2$	4-$CH_3C_6H_4$	3,4-$(OCH_3)_2C_6H_3$	C_6H_5	108–112		55	$CHCl_3$–MeOH
4o	$C_{26}H_{23}NO$	4-$CH_3C_6H_4$	4-$OCH_3C_6H_4$	4-$CH_3C_6H_4$	143–146		50	C_5H_5N–MeOH
4p	$C_{27}H_{26}N_2O$	4-$CH_3C_6H_4$	4-$N(CH_3)_2C_6H_4$	4-$OCH_3C_6H_4$	120–121		45	$CHCl_3$–MeOH
4q	$C_{26}H_{23}ClN_2$	4-$CH_3C_6H_4$	4-$N(CH_3)_2C_6H_4$	4-ClC_6H_4	130–139		50	C_5H_5N–MeOH
4r	$C_{26}H_{22}ClNO_2$	4-$CH_3C_6H_4$	3,4-$(OCH_3)_2C_6H_3$	4-ClC_6H_4	133–134		60	$CHCl_3$–MeOH
4s	$C_{25}H_{20}N_2O_3$	4-$CH_3C_6H_4$	4-$OCH_3C_6H_4$	3-$NO_2C_6H_4$	138–140		50	$CHCl_3$–MeOH
4t	$C_{26}H_{22}N_2O_4$	4-$CH_3C_6H_4$	3,4-$(OCH_3)_2C_6H_3$	3-$NO_2C_6H_4$	153–155		45	C_5H_5N–MeOH
4u	$C_{25}H_{20}ClNO$	4-$CH_3C_6H_4$	4-ClC_6H_4	4-$OCH_3C_6H_4$	112		50	C_5H_5N–MeOH

[a] Satisfactory elemental analyses were obtained for all compounds. [b] Reference 1. [c] Reference 8. [d] Reference 9.

Table II. NMR and IR Spectral Data for 2,4,6-Triaryl-Substituted Pyridines (4a–u)

	NMR data ($CDCl_3$),[a] ppm		IR data (KBr), cm^{-1}		
compd	aliphatic H	aromatic H	C–H str vibr	C=C vibr	C=N vibr
4a			3150	1595	1465
4b			3035	1600	1540
4c	6.04s, CH_2O_2	6.85–8.20m	3030	1595	1540
4d					
4e	2.35s, CH_3 3.85–3.95d, OCH_3	6.93–8.13m	2990	1595	1545
4f	2.40s, CH_3	7.20–8.16m			
4g	6.00s, CH_2O_2	6.96–8.10m			
4h	3.76s, OCH_3	6.80–8.00m			
4i	3.70–3.75d, OCH_3 ($J = 5$ Hz)	6.70–7.80m			
4j	2.40s, CH_3 3.85–3.90d, OCH_3 ($J = 5$ Hz)	7.03–8.20m			
4k	2.42s, CH_3 3.82s, OCH_3	6.90–8.38m	3040	1605	1545
4l	2.42s, CH_3	7.16–8.54m	3015	1600	1540
4m			3110	1601	1500
4n	2.34s, CH_3 3.78d, OCH_3	6.63–8.11m			
4o	2.62s, CH_3 3.98s, OCH_3	6.94–8.60m	3000	1605	1540
4p	2.76s, CH_3 3.88s, OCH_3	6.72–8.36m	2900	1590	1510
4q	2.82s, CH_3	6.80–8.32m	3015	1595	1525
4r			3020	1600	1490
4s			2940	1600	1520
4t			2990	1585	1520
4u	2.42s, CH_3 3.88s, OCH_3	6.98–8.32m			

[a] s = singlet, d = doublet, m = multiplet.

report here the synthesis of some 2,4,6-triaryl-substituted pyridines via phenacyl-β-picolinium ylide, 4-chlorophenacyl-γ-picolinium ylide, and 4-methylphenacyl-β-picolinium ylides.

Results and Discussion

Phenacyl-β-picolinium bromide (**1a**), 4-chlorophenacyl-γ-picolinium bromide (**1b**), and 4-methylphenacyl-β-picolinium bromide (**1c**) were prepared by quaternization of picolines with α-bromoacetophenones in almost 80% yields.

Various pyridines synthesized during this study, most of which are known to the literature, are listed in Table I. Their structures were supported by literature melting points, microanalyses which are in good accord with the calculated values, and spectral evidence (Table II).

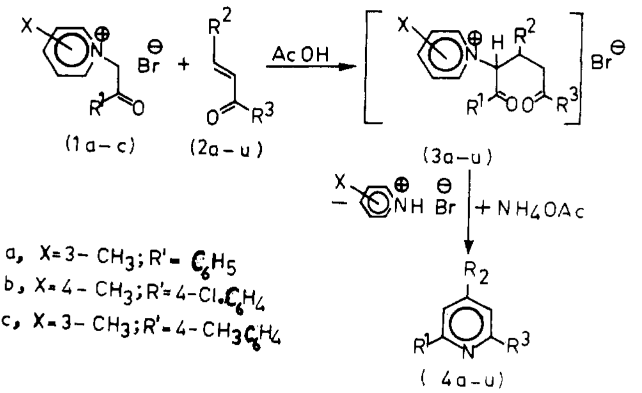
Experimental Section

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

Picolinium salts were prepared by the treatment of α-bromo ketones and picolines in benzene at reflux temperature.

Preparation of 2,4,6-Triaryl-Substituted Pyridines (4a–u). To a stirred solution of 3 mmol of picolinium salts (**1a–c**) in 10 mL of glacial acetic acid in the presence of ammonium acetate

Scheme I



was added gradually a solution of α,β-unsaturated ketones (**2a–u**, 3 mmol) in 30 mL of glacial acetic acid under an inert atmosphere of nitrogen. The mixture was then heated under reflux for 6–8 h, and then it was kept overnight at room temperature. On the next day, ice-cold water (50 mL) was added to it, and the precipitate thus obtained was separated, washed with methanol, dried, and recrystallized from an appropriate solvent mentioned in Table I to yield 2,4,6-triaryl-substituted pyridines (**4a–u**) (Scheme I).

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Correction

Aqueous Dissociation of Acetylenedicarboxylic Acid. Lowell M. Schwartz, Robert I. Gelb, and Daniel A. Laufer, *J. Chem. Eng. Data* **1980**, *25*, 95–6.

The first sentence inadvertently neglects to reference the more recent (1973) determination of acid dissociation constants at 25 °C reported by Pethybridge, A. D. *J. Chem. Soc., Perkin Trans. 2* **1973**, 102–4, who utilized the hydrogen-ion dependence of the rate of inversion of aqueous sucrose in order to calculate the concentrations of acetylenedicarboxylic acid species. Although this technique is markedly different from ours, he obtained $pK_{a1} = 0.664$ and $pK_{a2} = 2.365$ by assuming a Debye–Huckel ion-size parameter $a = 0.61$ nm for mean ionic activity coefficients, while we obtained $pK_{a1} = 0.656$ and $pK_{a2} = 2.336$ at 25 °C by using $a = 0.75$ nm. Considering that our values have estimated statistical uncertainties of ± 0.036 and ± 0.014 for pK_{a1} and pK_{a2}, respectively, and that assumptions about activity coefficients introduce systematic errors as well, the agreement between the two sets of results is gratifying.