

# Synthesis of Some New 2,4,6-Triaryl-Substituted Pyridines Via Aroylmethylenepyridinium Ylides

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A variety of 2,4,6-triaryl-substituted pyridines (Compounds 4a–8b) attached with naphthalene and thiophene rings are synthesized by the interaction of aroylmethylenepyridinium ylides with  $\alpha,\beta$ -unsaturated ketones. Ammonium acetate in acetic acid is used as the cyclization agent. Two alternative routes to synthesize pyridines (Compounds 4a–8b) are reported. The structural assignments of the products are based on ir and nmr spectral evidence.

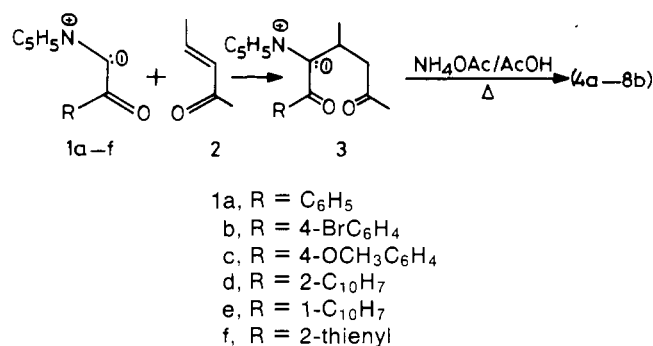
The reaction of phosphonium and sulfonium ylides with carbonyl compounds has been known for several years and has been extensively investigated and reviewed (5, 6, 9). However, the reaction of carbonyl stabilized pyridinium ylides with carbonyl compounds, particularly with  $\alpha,\beta$ -unsaturated ketones, has been relatively little explored until recently. Early developments in this reaction have been mainly reported by Krohnke (8), but no systematic work on the subject with spectral evidence has appeared in the literature so far.

In the present investigation we report the synthesis of a variety of 2,4,6-triaryl-substituted pyridines by the reaction mentioned above. The exploration of the studies is principally directed toward the synthesis of some new naphthalene and thiophene-substituted pyridine derivatives.

## Results and Discussion

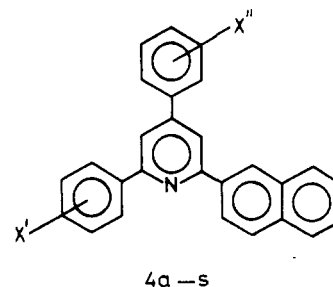
Heating the mixtures of aroylmethylenepyridinium ylides (Compounds 1a–f) with  $\alpha,\beta$ -unsaturated ketones (Compound 2) in the presence of ammonium acetate and glacial acetic acid at reflux temperature afforded 2,4,6-triaryl-substituted pyridines in 60–90% yields. The reaction seems to proceed via intermediacy of pentane-1,5-dionylpyridinium derivative (Compound 3) formed by the nucleophilic attack of ylide carbanion on the beta-carbon of Compound 2, which then undergoes cyclization in the presence of ammonium acetate to give the pyridines (Compounds 4a–8b) (Scheme 1).

Scheme 1



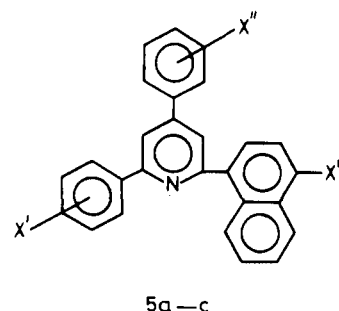
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**Route A.** Benzoylmethylenepyridinium ylides (Compounds 1a–c) underwent a smooth reaction with a variety of substituted benzylidene-2-acetonaphthones to give 2,4-diphenyl-6-(2-naphthyl)pyridines (Compounds 4a–s).



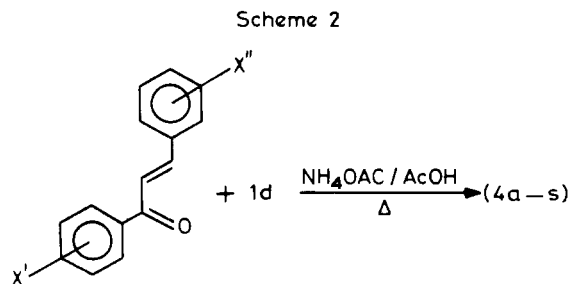
- 4 a, X' = H; X'' = H  
 b, X' = H; X'' = 4-OCH<sub>3</sub>  
 c, X' = H; X'' = 2-OCH<sub>3</sub>  
 d, X' = H; X'' = 3,4-OCH<sub>2</sub>O—  
 e, X' = H; X'' = 4-Cl  
 f, X' = H; X'' = 2,4-diCl  
 g, X' = 4-Br; X'' = H  
 h, X' = 4-Br; X'' = 4-NO<sub>2</sub>  
 i, X' = 4-Br; X'' = 4-Cl  
 j, X' = 4-Br; X'' = 4-OCH<sub>3</sub>  
 k, X' = 4-Br; X'' = 2-OCH<sub>3</sub>  
 l, X' = 4-Br; X'' = 3,4-OCH<sub>2</sub>O—  
 m, X' = 4-Br; X'' = 3,4-diOCH<sub>3</sub>  
 n, X' = 4-Br; X'' = 2,4-diCl  
 o, X' = 4-OCH<sub>3</sub>; X'' = H  
 p, X' = 4-OCH<sub>3</sub>; X'' = 4-NO<sub>2</sub>  
 q, X' = 4-OCH<sub>3</sub>; X'' = 4-Cl  
 r, X' = 4-OCH<sub>3</sub>; X'' = 2,4-diCl  
 s, X' = 4-OCH<sub>3</sub>; X'' = 4-OCH<sub>3</sub>

When the ylide 1b was allowed to react with 1-(benzylideneacetyl)-4-methoxynaphthalenes, pyridines 5b–c were isolated. Similarly, the ylide 1e reacted energetically with benzylideneacetophenone to give the similar type of pyridine 5a.

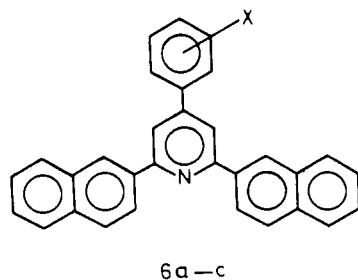


- 5a, X' = H; X'' = H; X''' = H  
 b, X' = 4-Br; X'' = H; X''' = —OCH<sub>3</sub>  
 c, X' = 4-Br; X'' = 4-NO<sub>2</sub>; X''' = —OCH<sub>3</sub>

**Route B.** It is interesting that the pyridines 4a-s are preparable by an alternative route, which involves the interaction of 2-naphthoyl ylide (Compound 1d) with benzylideneacetophenones (Scheme 2) instead of using phenacyl ylides (Compounds 1a-c) with benzylidene-2-acetonaphthones.

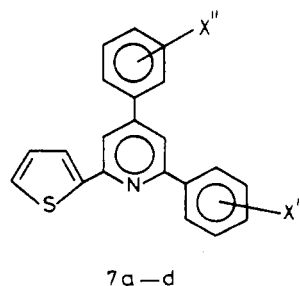


An extension of the above reaction in the synthesis of the 2,6-dinaphthylpyridine system was also successful when the ylide 1d was made to react with benzylidene-2-acetonaphthones in the presence of ammonium acetate. The 2,6-di-(2-naphthyl)-4-phenylpyridines (Compounds 6a-c) were obtained in good yields.

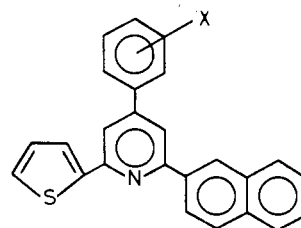


- 6a, X = H  
 b, X = 4-NO<sub>2</sub>  
 c, X = 3,4-OCH<sub>2</sub>O—

Next, attention was directed toward the synthesis of thiophene-substituted pyridine derivatives (Compounds 7 and 8). The synthesis of pyridines 7 and 8 was also achieved by two alternative routes (A and B). The first route (A) involves the interaction of ylides (Compounds 1a-c) with benzylidene-2-acetothiophenes. In the second procedure (Route B), the ylide 1f was allowed to react with benzylideneacetophenones and benzylideneacetona-phthones to give pyridines 7 and 8, respectively.



- 7a, X' = 4-Br; X'' = H  
 b, X' = 4-Br; X'' = 4-Cl  
 c, X' = 4-Br; X'' = 3,4-OCH<sub>2</sub>O—  
 d, X' = 4-OCH<sub>3</sub>; X'' = 4-NO<sub>2</sub>



8a-b

- 8a, X = 2-CH<sub>3</sub>  
 b, X = 4-OCH<sub>3</sub>

Various pyridines (Compounds 4a-8b) synthesized in this study are listed along with the best yields obtained in Table I. The applicability of the synthesis is obvious from the inspection of Table I. The best results are obtained when the electronegative group is attached at the para-position of the phenyl rings of benzylideneacetone. All the products synthesized as above gave satisfactory elemental analysis results. The structures of the products were supported by ir and nmr spectroscopy (Table II).

The ir absorption spectra (Table II) of the pyridines (Compounds 4a-8b) showed a characteristic absorption band in the region 3000-3077 cm<sup>-1</sup>, which is assigned to the CH stretching mode of pyridine rings (7). Two bands in the region 1600 and 1500 cm<sup>-1</sup> are assigned to the interactions between C=C and C=N vibrations of the pyridine rings. The former band, appearing as a double absorption maxima near 1600 cm<sup>-1</sup>, appears to be a general characteristic of trisubstitution at the pyridine nucleus (2). Bands owing to ring vibrations and CH-deformations absorbed near 1245 and 1020 cm<sup>-1</sup>, respectively. The chemical shifts in the nmr spectra of 2,4,6-tri-substituted pyridines (Compounds 4a-8b), exhibited two pyridyl protons (singlet) in the range of  $\delta$  7.03-7.33 and an aromatic multiplet in the range of  $\delta$  7.20-8.48.

### Experimental

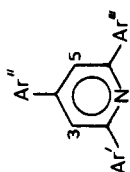
Melting points were determined on a Gallenkamp apparatus and are uncorrected. A Perkin-Elmer infracord spectrophotometer was used to determine the ir spectra (KBr). The nmr spectra (CDCl<sub>3</sub>) were run by use of a Varian A-60 spectrometer with tetramethylsilane as the internal standard. Column chromatography was done to purify the products, by use of a glass column packed with neutral alumina. For thin-layer chromatography (tlc), glass microscope slides coated with silica gel G were used. The spots on these slides were detected by iodine.

Pyridinium salts were prepared by treatment of the pyridine with  $\alpha$ -bromoketones or by heating methyl ketones with iodine and pyridine by use of the procedure of King (7). Pyridinium ylides (Compounds 1a-f) were prepared by treating cold aqueous solutions of pyridinium salts with cold aqueous potassium carbonate or by treating pyridinium salts with sodium hydride in dimethylformamide solvent, according to the procedure of Henrick et al. (4). Benzylideneacetones were prepared by the reaction of arylmethyl ketones with aromatic aldehydes in the presence of alcoholic sodium hydroxide by use of the procedure given elsewhere (3).

**General procedure for preparation of 2,4,6-triaryl-substituted pyridines (Compounds 4a-8b).** Three general routes (A, B, and C) were employed.

**Route A.** A stirred mixture of arylmethylpyridinium ylide (Compounds 1a-f) (3 mmol) and ammonium acetate (3 grams) in glacial acetic acid (25 ml) was treated by dropwise addition with the benzylideneacetone (3

Table 1. Structure and Physical Properties of 2,4,6-Triaryl-Substituted Pyridines (Compounds 4a-8b)



4a-8b

Com- pound	Molecular formula	Ar'	Ar''	Ar'''	Ylide used	Rte of prep- aration	Mp, °C	Yield, %	Crystallization solvent	Anal. data* Found/Calcd, %			
										C	H	N	
4a	C <sub>27</sub> H <sub>19</sub> N	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	2-Naphthyl	1a	A	120-122 <sup>b</sup>	70	C <sub>3</sub> H <sub>7</sub> N-MeOH (1:3)	90.72 90.75	5.30 5.32	3.90 3.92	
4b	C <sub>28</sub> H <sub>21</sub> NO	C <sub>6</sub> H <sub>5</sub>	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2-Naphthyl	Salt <sup>c</sup>	C	120-122	40	EtOH-H <sub>2</sub> O (1:2)		86.78 86.82	5.39 5.42	3.55 3.61
					1d	B	121-122	64					
					1a	A	130	67					
4c	C <sub>28</sub> H <sub>21</sub> NO	C <sub>6</sub> H <sub>5</sub>	2-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1d	B	131	62	MeOH-H <sub>2</sub> O (1:2)	86.79 86.82	5.42 5.42	3.60 3.61	
					1a	A	115	65					
4d	C <sub>28</sub> H <sub>19</sub> NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	3,4-O <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	2-Naphthyl	Salt <sup>c</sup>	C	113-115	34	EtOH (90%)	83.77 83.79	4.14 4.13	3.50 3.49	
					1a	A	128-130	60					
4e	C <sub>27</sub> H <sub>18</sub> NCl	C <sub>6</sub> H <sub>5</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1a	A	125-126	74	C <sub>3</sub> H <sub>7</sub> N-MeOH (1:4)	82.77 82.76	4.58 4.59	3.05 3.07	
					1d	B	124-126	65					
4f	C <sub>27</sub> H <sub>17</sub> NCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	2,4-dichloroC <sub>6</sub> H <sub>3</sub>	2-Naphthyl	Salt <sup>c</sup>	C	124-126	40	CHCl <sub>3</sub> -MeOH (1:4)	83.74 83.73	3.98 3.98	2.28 2.29	
					1a	A	118-121	58					
4g	C <sub>27</sub> H <sub>18</sub> NBr	4-BrC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	2-Naphthyl	1b	A	122-124	74	C <sub>3</sub> H <sub>7</sub> N-MeOH (1:4)	74.32 74.32	4.17 4.19	3.22 3.21	
					1d	B	122-124	70					
4h	C <sub>27</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> Br	4-BrC <sub>6</sub> H <sub>4</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	2-Naphthyl	Salt <sup>d</sup>	C	122-124	40	MeOH-H <sub>2</sub> O (1:4)	67.34 67.31	5.53 5.53	5.85 5.84	
					1b	A	232-238	90					
4i	C <sub>27</sub> H <sub>17</sub> NCIBr	4-BrC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1d	B	235-238	87	C <sub>3</sub> H <sub>7</sub> N-MeOH (1:3)	68.85 68.88	3.59 3.61	2.98 2.97	
					1b	A	150-152	85					
4j	C <sub>28</sub> H <sub>20</sub> NOBr	4-BrC <sub>6</sub> H <sub>4</sub>	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1b	A	138-140	70		72.11 72.12	4.28 4.29	3.01 3.00	
					1b	A	117-120	67					
4k	C <sub>28</sub> H <sub>20</sub> NOBr	4-BrC <sub>6</sub> H <sub>4</sub>	2-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1b	A	122-125	65	C <sub>3</sub> H <sub>7</sub> N-EtOH (1:1)	70.00 70.02	3.72 3.75	2.93 2.92	
					1b	A	140-142	60					
4l	C <sub>28</sub> H <sub>22</sub> NO <sub>2</sub> Br	4-BrC <sub>6</sub> H <sub>4</sub>	3,4-O <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	2-Naphthyl	1b	A	140-142	60	C <sub>3</sub> H <sub>7</sub> N-EtOH-H <sub>2</sub> O (1:3:1)	70.12 70.11	4.44 4.43	2.85 2.89	
					1b	A	140-142	60					

4n	C <sub>27</sub> H <sub>16</sub> NCl <sub>2</sub> Br	4-BrC <sub>6</sub> H <sub>4</sub>	2,4-diClC <sub>6</sub> H <sub>3</sub>	2-Naphthyl	1b	A	170-172	66	C <sub>3</sub> H <sub>5</sub> N-MeOH (1:4)	60.22	3.12	2.79
4o	C <sub>28</sub> H <sub>21</sub> NO	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	2-Naphthyl	1c	A	105-110	62	C <sub>3</sub> H <sub>5</sub> N-H <sub>2</sub> O (1:3)	60.21	3.16	2.77
4p	C <sub>28</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1d	B	106-110	62	C <sub>3</sub> H <sub>5</sub> N-MeOH (1:2)	86.55	5.40	3.61
4q	C <sub>28</sub> H <sub>20</sub> NOCl	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1c	A	195-197	75		86.56	5.42	3.61
4r	C <sub>28</sub> H <sub>19</sub> NOCl <sub>2</sub>	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2,4-diClC <sub>6</sub> H <sub>3</sub>	2-Naphthyl	1d	B	196-197	73		75.45	4.61	6.46
4s	C <sub>29</sub> H <sub>23</sub> NO <sub>2</sub>	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1c	A	153-154	70		75.46	4.62	6.47
5a	C <sub>27</sub> H <sub>19</sub> N	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	1-Naphthyl	1d	B	123-124	62	MeOH-H <sub>2</sub> O (1:4)	90.74	5.30	3.91
5b	C <sub>28</sub> H <sub>20</sub> NOBr	4-BrC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	1-(4-OCH <sub>3</sub> naphthyl)	1e	B	125-128 <sup>a</sup>	56		90.72	5.32	3.92
5c	C <sub>28</sub> H <sub>19</sub> N <sub>2</sub> O <sub>3</sub> Br	4-BrC <sub>6</sub> H <sub>4</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	1-(4-OCH <sub>3</sub> naphthyl)	1a	A	170-172	55		72.08	4.24	3.00
6a	C <sub>31</sub> H <sub>21</sub> N	2-Naphthyl	C <sub>6</sub> H <sub>5</sub>	2-Naphthyl	1b	A	150	62	C <sub>3</sub> H <sub>5</sub> N-EtOH (1:4)	72.12	4.27	3.00
6b	C <sub>31</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	2-Naphthyl	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1b	A	200	67	MeOH-H <sub>2</sub> O (1:2)	65.91	3.71	5.68
6c	C <sub>32</sub> H <sub>21</sub> NO <sub>2</sub>	2-Naphthyl	3,4-O <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	2-Naphthyl	1d	B	196-200 <sup>f</sup>	55	EtOH (90%)	65.95	3.71	5.67
7a	C <sub>21</sub> H <sub>14</sub> NSBr	2-Thienyl	C <sub>6</sub> H <sub>5</sub>	4-BrC <sub>6</sub> H <sub>4</sub>	1d	B	240-242	60	CHCl <sub>3</sub> -MeOH (1:4)	91.40	5.13	3.44
7b	C <sub>21</sub> H <sub>13</sub> NSClBr	2-Thienyl	4-ClC <sub>6</sub> H <sub>4</sub>	4-BrC <sub>6</sub> H <sub>4</sub>	1b	A	142-143	62	C <sub>3</sub> H <sub>5</sub> N-EtOH (1:4)	82.29	4.45	6.16
7c	C <sub>22</sub> H <sub>14</sub> NO <sub>2</sub> SBr	2-Thienyl	3,4-O <sub>2</sub> CH <sub>2</sub> C <sub>4</sub> H <sub>3</sub>	4-BrC <sub>6</sub> H <sub>4</sub>	1b	A	138-140	70	C <sub>3</sub> H <sub>5</sub> N-EtOH (1:4)	82.27	4.43	6.19
7d	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> S	2-Thienyl	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	1f	B	145-148	68	C <sub>3</sub> H <sub>5</sub> N-MeOH (1:2)	85.14	4.65	3.10
8a	C <sub>26</sub> H <sub>19</sub> NS	2-Thienyl	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1c	A	157-160	70		64.32	3.52	7.05
8b	C <sub>26</sub> H <sub>19</sub> NOS	2-Thienyl	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2-Naphthyl	1f	B	170-172	30	CHCl <sub>3</sub> -MeOH (1:2)	64.30	3.54	7.08

<sup>a</sup> Satisfactory analytical data ( $\pm 0.4\%$  for C, H, N) were reported for all compounds listed in the table. <sup>b</sup> Lit. (10) mp 124°C. <sup>c</sup> Salt of 1a, i.e., phenacylpyridinium bromide. <sup>d</sup> Salt of 1b, i.e., p-mophenacylpyridinium bromide. <sup>e</sup> Lit. (10), mp 122°C. <sup>f</sup> Lit. (10), mp 204°C.

**Table II. Ir and Nmr Data for 2,4,6-Triaryl-Substituted Pyridines<sup>a</sup> (Compounds 4a-8b)**

Compound	Ir data (KBr), cm <sup>-1</sup>						Nmr data (CDCl <sub>3</sub> ); δ, ppm		
	CH stretch- ing vibrations	C=C and C=N vibrations		Ring vibrations, CH— deformations		Aliphatic H	Pyridyl H	Aromatic H	
4a	3049	1603	1560	1502	1241	1035	...	7.05 s	7.52-8.30 m
4b	3004	1600	1538	1506	1250	1026	3.95 s, OCH <sub>3</sub>	7.22 s	7.59-8.43 m
4c	3012	1608	1546	1488	1247	1024	...	...	...
4d	3000	1600	1553	1504	1252	1047	6.13 s, —OCH <sub>2</sub> O—	7.10 s	7.50-8.26 m
4e	3003	1603	1541	1502	1242	1012	...	...	...
4f	3021	1605	1575	1548	1212	1009	...	...	...
4g	3012	1600	1546	1488	1239	1011	...	...	...
4h	3049	1608	1553	1490	1242	1015	...	...	...
4i	3058	1610	1583	1495	1244	1011	...	...	...
4j	3040	1608	1553	1520	1259	1011	3.86 s, OCH <sub>3</sub>	7.13 s	7.26-8.30 m
4k	3021	1603	1541	1491	1244	1009	...	...	...
4l	3021	1600	1548	1502	1250	1009	6.03 s, —OCH <sub>2</sub> O—	7.03 s	7.23-8.30 m
4m	3040	1603	1541	1517	1272	1027	4.00 s, OCH <sub>3</sub>	7.26 s	7.43-8.23 m
4n	3000	1600	1543	1475	1238	1009	...	...	...
4o	...	...	...	...	...	...	3.83 s, OCH <sub>3</sub>	7.13 s	7.46-8.40 m
4p	3003	1603	1546	1511	1255	1024	3.93 s, OCH <sub>3</sub>	7.04 s	7.20-8.37 m
4q	3003	1595	1541	1506	1250	1026	3.83 s, OCH <sub>3</sub>	7.10 s	7.50-8.26 m
4r	3021	1603	1572	1548	1218	1012	3.94 s, OCH <sub>3</sub>	7.33 s	7.50-8.40 m
4s	...	...	...	...	...	...	3.86 s, OCH <sub>3</sub>	7.08 s	7.70-8.33 m
5a	3030	1595	1560	1508	1250	1026	...	7.08 s	7.50-8.30 m
5b	...	...	...	...	...	...	4.10 s, OCH <sub>3</sub>	7.06 s	7.53-8.33 m
5c	3021	1592	1543	1511	1220	1012	4.02 s, OCH <sub>3</sub>	7.20 s	7.50-8.26 m
6a	3040	1597	1546	1484	1236	1021	...	...	...
6b	3012	1590	1522	1488	1227	1009	...	...	...
6c	...	...	...	...	...	...	6.03 s, —OCH <sub>2</sub> O—	7.03 s	7.26-8.33 m
7a	3040	1616	1546	1495	1244	1011	...	...	...
7b	3021	1597	1543	1490	1241	1009	...	...	...
7c	3003	1603	1543	1502	1256	1004	6.00 s, —OCH <sub>2</sub> O—	7.10 s	7.36-8.13 m
7d	3077	1629	1563	1527	1235	1026	3.93 s, OCH <sub>3</sub>	7.08 s	7.73-8.40 m
8a	3021	1603	1546	1495	1225	1016	2.33 s, CH <sub>3</sub>	7.30 s	7.53-8.33 m
8b	...	...	...	...	...	...	3.86 s, OCH <sub>3</sub>	7.16 s	7.50-8.48 m

<sup>a</sup> s = singlet, m = multiplet.

mmol) in glacial acetic acid (10 ml) at reflux temperature (110–120°) in the current of nitrogen. After complete addition the resulting mixture was heated under reflux for an additional 3 hr, cooled, and then the 2,4,6-tri-substituted pyridine was precipitated by addition of cold water (20 ml). The precipitated solid was separated, washed with methanol, and crystallized from an appropriate solvent to give the crystalline products in appreciable yields (Table I).

**Route B.** This procedure is the same as above except methanol was used as solvent in place of glacial acetic acid. This route has proved to be more favorable for the synthesis of 2,6-dinaphthylpyridine derivatives (Compounds 6a–c).

**Route C (direct method).** A mixture of aroylmethylpyridinium salt (3 mmol), benzylideneacetone (Compound 2) (3 mmol), ammonium acetate (3 grams), and glacial acetic acid (20 ml) was heated under reflux with stirring for 3 hr in an inert atmosphere of nitrogen. The reaction mixture was cooled, and the 2,4,6-triaryl-substituted pyridine was precipitated by addition of water. The precipitate was separated and crystallized from a suitable solvent. Although this procedure is more convenient than those of procedures A and B, formation of a blackish by-

product generally creates difficulty in separating and purifying the 2,4,6-tri-substituted pyridines and lowers the yields to a great extent.

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