Studies on Ylides: Reactions of N-Pyridinium Phenacylides with 
α,β-Unsaturated Ketones, I

Synthesis of 2,4,6-Triarylsubstituted Pyridines

PUSHOTTAM S. KENDURKAR and RAM S. TEWARI

Department of Chemistry, Harcourt Butler Technological Institute, Kanpur-2, India

(Z. Naturforsch. 29b. 552-555 [1974]; received January 17/April 16, 1974)

Ylides, N-pyridinium, Phenacylide, Ketones

Reactions of N-pyridinium phenacylides with different α,β-unsaturated ketones give 2,4,6-triarylsubstituted pyridines, 2,6-diphenyl-4-(2-pyridyl) pyridines, 2-benzylidene-4,6-diphenyl pyridines and 2,4,6-triphenyl-3-bromopyridine. Ammonium acetate in acetic acid was used as cyclization agent. The structure of the products are supported by IR and NMR spectra.

Our interest in the reactivity of P- and As-ylides towards carbonyl substrates prompted us to carry out studies on the reactivity of N-ylides with α,β-unsaturated ketones.

Although Krohnke et al.3 have reported such type of reactions using pyridinium salts but it could not be duplicated until recently. With a view to explore the studies on the reactivity of pyridinium ylides toward α,β-unsaturated ketones we have studied the reactions of N-pyridinium phenacylides with different α,β-unsaturated ketones.

Results and Discussion

N-pyridinium phenacylides (1a–d) reacted with variety of substituted benzylidene acetophenones (2) in refluxing glacial acetic acid to afford 2,4,6-triarylsubstituted pyridines (4a–r), presumably via 1,5-dionylpyridinium derivatives (3a–r)3 (Scheme 1).

![Scheme 1](image)

Similarly when the ylides (1e,d) were allowed to react with 2-pyridylidene acetophenone (2, C₆H₄-R''=2-C₆H₄N; R''=4-Br), pyridines (5a,b) were isolated in 60–62% yields.

Requests for reprints should be sent to Dr. R. S. Tewari, Department of Chemistry, Harcourt Butler Technological Institute, Kanpur-2, India.
When the ylides (1a,d) were made to react with dibenzylidene acetone (6) 2-stilbazoles (7a,b) were obtained analogously (Scheme 2).

\[ 1a,d + \text{NH}_2\text{OAc/ACOH} \xrightarrow{\Delta} 7a, 7b \]

Scheme 2

All the pyridines synthesized in this study are listed in Table I. The general applicability of the synthesis is obvious from the inspection of Table I.

Table I. 2,4,6-Triaryls substituted pyridines ((4a–r)–9).
Table II. NMR spectra (CDCl₃) of 2,4,6-triarylsubstituted pyridines.

<table>
<thead>
<tr>
<th>Product</th>
<th>δ [ppm]</th>
<th>Number of protons</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>4b</td>
<td>7.30–8.42, m</td>
<td>13H Pheny1</td>
<td></td>
</tr>
<tr>
<td>7.08, s</td>
<td>2H Pyridyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.08, s</td>
<td>2H –OCH₂O–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4i</td>
<td>7.50–8.41, m</td>
<td>13H Pheny1</td>
<td></td>
</tr>
<tr>
<td>7.13, s</td>
<td>2H Pyridyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.90, s</td>
<td>6H Two OCH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7b</td>
<td>7.35–8.40, m</td>
<td>14H Pheny1</td>
<td></td>
</tr>
<tr>
<td>7.14, s</td>
<td>2H Pyridyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.86, q</td>
<td>2H –CH = CH–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>7.45–8.44, m</td>
<td>13H Pheny1</td>
<td></td>
</tr>
<tr>
<td>7.10, s</td>
<td>1H Pyridyl</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

m = multiplet; s = singlet; q = quartet.

Pyridinium ylides (1a–d) were prepared by treating cold aqueous solution of pyridinium salt with aqueous potassium carbonate or by treating pyridinium salts with sodium hydride in dimethylformamide solvent, according to the procedure of Henrick et al. All the reactions were carried out with freshly prepared pyridinium ylides.

Preparation of 2,4,6-triarylsubstituted pyridines (4a–r–5b). (Table I)

A general procedure was used in all the reactions. A mixture of N-pyridinium phenacylides (1a–d) (0.003 mole) and ammonium acetate (3 g) in glacial acetic acid was stirred at 80 °C. Benzylidene ketone (2) (0.003 mole) in glacial acetic acid (10 ml) was added dropwise during 1 h, after which time the temperature was allowed to rise to 120 °C and heating was continued for additional 3 h. The mixture was left overnight at room temperature and ice-cold water (20 ml) was added to precipitate a solid which was separated, washed with methanol and crystallized from appropriate solvent to yield 2,4,6-trisubstituted pyridine.

Preparation of 2-benzylidene-4,6-diphenyl pyridines (7a–b). (Table I)

Same procedure was used, except dibenzylideneacetone (6) was used instead of benzylidene ketone.

Preparation of 2,6-di-(4-bromophenyl)-4-phenyl-3-bromo pyridine (9). (Table I)

Above procedure was used, except a-bromobenzylidene acetophenone (8) was used in place of benzylidene ketone.

The authors wish to thank Dr. S. D. Shukla, Director and Professor R. C. Srivastava, H. B. Technological Institute, Kanpur-2, for providing facilities. PSK is thankful to the CSIR, New Delhi, for the award of a Senior Research Fellowship.

4 L. C. King, J. Amer. chem. Soc. 66, 894 [1964].