The First Approach to the Synthesis of 1-Unsubstituted 2-Arylindolizines by Intramolecular 1,5-Dipolar Cyclization of 2-(2-Arylethenyl)pyridinium Ylides in the Presence of Tetrakis(pyridine)cobalt (II) Dichromate

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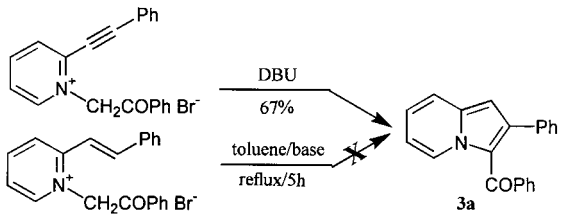
Abstract: The first approach to the preparation of 1-unsubstituted 2-arylindolizines by intramolecular 1,5-dipolar cyclization of 2-(2-arylethenyl)pyridinium ylides **2a–v** in the presence of tetrakis(pyridine)cobalt (II) dichromate was developed. Several kinds of novel 1-unsubstituted 2-aryl-3-acetyl-, 3-benzoyl-, 3-ethoxycarbonyl- and 3-(4-nitrobenzoyl)indolizines **3a–v** were synthesized under the mild conditions in reasonable to moderate yields.

Key words: 1-unsubstituted 2-arylindolizines, intramolecular 1,5-dipolar cyclization, pyridinium ylides, tetrakis(pyridine)cobalt (II) dichromate

Perhydro derivatives of indolizine occurr in natural products.[1,2] However, indolizines with discrete aromatic nucleus could be synthesized only in laboratories. For both theoretical and practical reasons, synthetic indolizines have attracted special attention in past years.[1,3] Many of them have been used as photographic sensitisers,[1b,4] biological markers[5] and potential candidates for pharmaceutical researches.[6] A Japanese group recommended 1-methoxycarbonylindolizine-3,5-dicarbaldehyde as a derivatization reagent for amino compounds in high-performance capillary electrophoresis (HPCE).[7]

In continuation of our research project to find bioactive heterocyclic compounds as potential candidates in agricultural chemistry, a series of 1-unsubstituted 2-arylindolizines **3** was designed as target compounds for synthesis. The methods for preparation of indolizines were summarized in several reviews[1,8] and some new procedures were reported very recently.[9] Among them, Tschitschibabin reaction[10] and intramolecular 1,5-dipolar cycloaddition of pyridinium *N*-allylides[11] can introduce an aryl group to C-2 in indolizine conveniently. But the methods were limited seriously for our purpose because the reaction mechanism required a functional group other than hydrogen on C-1 in indolizine for the most cases.

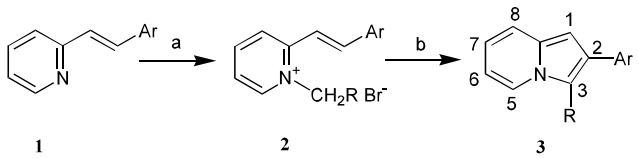
The best method to prepare the desired 2-arylindolizines is the Tsuchiya's procedure,[12] exemplified by the synthesis of 2-phenyl-3-benzoylindolizine (**3a**) by the thermal intramolecular 1,5-dipolar cyclization of 2-(2-phenylethynyl)pyridinium *N*-ylide in 67% yield (Scheme 1). However, the fact that 2-arylindolizines are not prepared any more by this procedure may be due to the fact that most of the derivatives of 2-(2-phenylethynyl)pyridine



Scheme 1

are not commercially available and also not convenient to prepare in the laboratories. Herein we report a new approach for the preparation of 1-unsubstituted 2-arylindolizines by intramolecular 1,5-dipolar cyclization of 2-(2-arylethenyl)pyridinium ylides in the presence of tetrakis(pyridine)cobalt (II) dichromate (TPCD).

TPCD, a bimetallic coordination compound, is a mild and versatile oxidant,[13] and is used widely in organic synthesis.[14] In our previous papers,[15] alkenes instead of alkynes were used successfully in a 1,3-dipolar cycloaddition reaction with pyridinium ylides to prepare indolizines in the presence of TPCD. These results persuaded us to try to modify Tsuchiya's procedure by using 2-(2-phenylethenyl)pyridinium *N*-ylide (from pyridinium salt **2a**) instead of 2-(2-phenylethynyl)pyridinium *N*-ylide. As expected, no desired product was detected in the absence of TPCD after a solution of **2a** and triethylamine in toluene was refluxed for 5 hours (Scheme 1). However, when equimolar amounts of TPCD was added to the reaction mixture, **2a** was converted smoothly to the corresponding indolizine **3a** (Scheme 2).



1	Ar	1	Ar
a	C_6H_5	**d**	3,4-$Cl_2C_6H_3$
b	2-ClC_6H_4	**e**	4-$NO_2C_6H_4$
c	4-ClC_6	**f**	4-$MeOC_6H_4$

Reagents and conditions: (a) $RCH_2Br/CHCl_3$, 50–60 °C (79–96%); (b) TPCD/Et_3N/toluene, 80–90 °C (17–54%)

Scheme 2

2-(2-Arylethenyl)pyridines **1a–f** were prepared by known procedures[16] and were converted to their corresponding pyridinium salts **2a–2v** in high yields simply by the addition of equimolar amounts of appropriate bromides to a chloroform solution of **1** at 50–60 °C. In the case of **2n**, ethyl acetate was used as a solvent to give a powder salt (Tables 1 and Table 2). Unfortunately, all attempts to prepare 2,6-bis(2-phenylethenyl)pyridinium and 2-(2-phenylethenyl)quinolinium salts from the corresponding 2,6-bis(2-phenylethenyl)pyridine and 2-(2-phenylethenyl)-quinoline, respectively, failed.

Table 1 Pyridinium Salts **2a–v** and Indolizines **3a–v** Prepared

Products	R	Ar	Yields (%)[a]	
			2	**3**
a	COC_6H_5	C_6H_5	92	19
b	COC_6H_5	2-ClC_6H_4	89	18
c	COC_6H_5	4-ClC_6H_4	94	44
d	COC_6H_5	3,4-$Cl_2C_6H_3$	85	22
e	COC_6H_5	4-$NO_2C_6H_4$	87	20
f	COC_6H_5	4-$MeOC_6H_4$	90	25
g	COMe	C_6H_5	85	28
h	COMe	2-ClC_6H_4	96	21
i	COMe	4-ClC_6H_4	79	37
j	COMe	3,4-$Cl_2C_6H_3$	89	54
k	COMe	4-$NO_2C_6H_4$	81	44
l	COMe	4-$MeOC_6H_4$	84	21
m	CO_2Et	C_6H_5	80	18
n	CO_2Et	2-ClC_6H_4	90	17
o	CO_2Et	4-ClC_6H_4	85	19
p	CO_2Et	3,4-$Cl_2C_6H_3$	88	27
q	CO_2Et	4-$NO_2C_6H_4$	92	20
r	CO_2Et	4-$MeOC_6H_4$	87	17
s	4-$NO_2C_6H_4$	C_6H_5	83	21
t	4-$NO_2C_6H_4$	2-ClC_6H_4	84	26
u	4-$NO_2C_6H_4$	4-ClC_6H_4	80	23
v	4-$NO_2C_6H_4$	3,4-$Cl_2C_6H_3$	86	31

[a] Yield based on the isolated product.

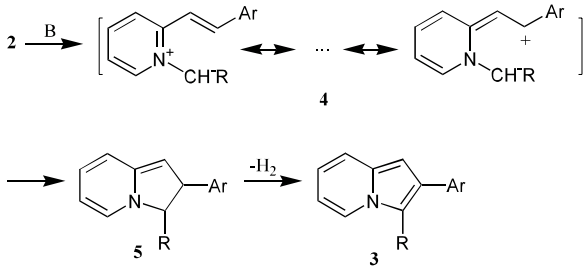
Table 2 2-(2-Arylethenyl)pyridinium Salts **2a–v** Prepared

Product	mp (°C)	IR (KBr) ν (cm^{-1})	Product	mp (°C)	IR (KBr) ν (cm^{-1})
2a	230–236	1687, 1616	**2l**	194–196	1729, 1602
2b	237–240	1687, 1616	**2m**	185–186	1743, 1623
2c	206–210	1687, 1616	**2n**	186–188	1743, 1616
2d	235–237	1687, 1616	**2o**	198–200	1750, 1623
2e	78	1687, 1595	**2p**	200–202	1750, 1616
2f	202–206	1687, 1602	**2q**	182–184	1736, 1616
2g	206–208	1687, 1623	**2r**	180–182	1743, 1602
2h	146–148	1729, 1616	**2s**	234–236	1609, 1518
2i	210–212	1722, 1609	**2t**	229–231	1609, 1518
2j	193–195	1729, 1616	**2u**	232–234	1623, 1525
2k	210–213	1722, 1609	**2v**	230–232	1616, 1518

Under the standard conditions, a stirred suspension of pyridinium salts **2a–v**, triethylamine, and TPCD in toluene was heated at 80–90 °C for 4–6 hours (monitored by TLC). After the solid was filtered off and toluene was evaporated, the corresponding indolizines **3a–v** were obtained in 17–54% yields (Tables 1 and 3). The reaction conditions is very mild and workup procedure is convenient. It is worthy to note that the use of excess TPCD has no effect in increasing the yields of the products. Use of DMF as a solvent reduced the yields and made the workup procedure tedious.

The experimental results proved that the aryl group on the double bond in 2-vinylpyridine and the presence of TPCD are necessary for the reaction. For example, the parent 2-vinylpyridinium salt just gave an unidentified product mixture and none of components used to prepare TPCD, such as chromium trioxide or cobalt (II) acetate did show any activity by themselves.

The ylide **4** is formed in the initial step of the reaction with certainty when the salt **2** is treated with triethylamine. We assume that one of the resonance structures of the ylide **4** functions as a 1,5-dipole and may be expected to undergo 1,5-dipolar cyclization to afford dihydroindolizines **5**, which could be aromatized in situ by TPCD to yield indolizines **3** (Scheme 3). The fact that dihydroindolizines can be aromatized easily to give the corresponding indolizines by TPCD[15b] supports this mechanism. However, none of the intermediate dihydroindolizines **5** were detected or separated in the above reactions so far.



Scheme 3

In conclusion, the first procedure of intramolecular 1,5-dipolar cyclization of 2-(2-arylethenyl)pyridinium ylides **2a–v** effected by TPCD was developed. The reaction using alkenes instead of alkynes as starting materials provides a convenient and general method for the preparation of 1-unsubstituted 2-arylindolizines, which are quite difficult to prepare by any other published method.

All melting points were determined on a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet FT-IR 5DX spectrometer with KBr pellets. ^{1}H NMR spectra were recorded on a Bruker ACF-300 spectrometer with TMS as internal reference. *J* Values are given in Hz. MS spectra were obtained on a ZAB-HS mass spectrometer with 70 eV. Elemental analyses were performed on a Perkin-Elmer 240C instrument.

2-(2-Arylethenyl)pyridinium Salts 2a–v; General Procedure

A mixture of 2-(2-arylethenyl)pyridine **1** (20 mmol) and the appropriate bromide (20 mmol) in $CHCl_3$ (15 mL) was allowed to stand overnight at r.t. and then was stirred at 50–60 °C for several hours. The precipitated 2-(2-arylethenyl)-pyridinium salts **2** (79–96%) were collected by filtration and washed with $CHCl_3$ (3 × 5 mL). They were used in the next step directly without further purification.

Table 3 1-Unsubstituted 2-Arylindolizines **3a–v** Prepared

Product[a]	Color	mp (°C)	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	MS (70 eV) *m*/*z* (%)
3a	yellow	137–138[b]	1588, 1497, 744, 695	9.81 (d, 1 H, *J* = 7.4), 7.54 (d, 1 H, *J* = 8.8), 7.41 (d, 2 H, *J* = 6.9), 7.16–6.88 (10 H, m), 6.58 (1 H, s)	297 (M^+, 100), 220 (45), 192 (23)
3b	yellow	140–142	1595, 1497, 787, 737, 695	9.83 (d, 1 H, *J* = 6.7), 7.69 (d, 1 H, *J* = 6.5), 7.58 (d, 2 H, *J* = 8.6), 7.44–6.91 (m, 9 H), 6.59 (s, 1 H)	333 (6), 331 (M^+, 17), 296 (100), 191 (91)
3c	yellow	89–90	1595, 1497, 801, 723, 702	9.80 (d, 1 H, *J* = 7.2), 7.55 (d, 1 H, *J* = 8.8), 7.39 (d, 2 H, *J* = 7.1), 7.21–7.16 (m, 2 H), 7.07–6.88 (m, 7 H), 6.93–6.88 (m, 1 H), 6.55 (s, 1 H)	333 (37), 331 (M^+, 100), 191 (65), 77 (52)
3d	yellow	169–171	1595, 1479, 865, 821, 744, 695	9.81 (d, 1 H, *J* = 6.7), 7.57 (d, 1 H, *J* = 8.6), 7.40 (d, 2 H, *J* = 7.0), 7.24–6.88 (m, 8 H), 6.97–6.88 (m, 2 H), 6.57 (s, 1 H)	369 (12), 367 (68), 365 (M^+, 100), 77 (41)
3e	yellow	236–237	1595, 1511, 1340, 746, 697	9.81 (d, 1 H, *J* = 6.4), 7.87 (d, 2 H, *J* = 8.5), 7.59 (d, 1 H, *J* = 7.0), 7.38 (d, 2 H, *J* = 8.6), 7.26–6.98 (m, 7 H), 6.63 (s, 1 H)	342 (M^+, 100), 77 (31)
3f	yellow	154–155	1581, 1497, 1335, 1244, 808, 752, 695	9.80 (d, 1 H, *J* = 6.5), 7.54 (d, 1 H, *J* = 8.5), 7.42 (d, 2 H, *J* = 7.1), 7.20–6.98 (m, 6 H), 6.90 (d, 1 H, *J* = 6.6), 6.55 (d, 3 H, *J* = 7.6), 3.70 (s, 3 H)	327 (M^+, 100), 77 (18)
3g	yellow	oil	1623, 1504, 1406, 744, 702	10.02 (d, 1 H, *J* = 6.8), 7.51–7.41 (m, 6 H), 7.15 (m, 1 H), 6.88 (m, 1 H), 6.48 (s, 1 H), 2.07 (s, 3 H)	235 (M^+, 45), 220 (54), 108 (100)
3h	yellow	94	3142, 3058, 1616, 1497, 1406, 1328, 752	10.01 (d, 1 H, *J* = 7.1), 7.55–6.90 (m, 7 H), 6.46 (s, 1 H), 2.02 (s, 3 H)	271 (8), 269 (M^+, 22), 234 (100)
3i	yellow	78–80	1602, 1497, 1420, 1391, 1328	9.98 (d, 1 H, *J* = 7.1), 7.51 (d, 1 H, *J* = 8.8), 7.44–6.87 (m, 6 H), 6.45 (s, 1 H), 2.07 (s, 3 H)	271 (33), 269 (M^+, 98), 254 (100), 219 (59), 191 (51)
3j	yellow	119–121	1609, 1497, 1413, 1370, 1328, 794	9.97 (d, 1 H, *J* = 7.1), 7.61 (s, 1 H), 7.52 (d, 2 H, *J* = 8.6), 7.28–6.92 (m, 3 H), 6.46 (s, 1 H), 2.10 (s, 3 H)	307 (11), 305 (66), 303 (M^+, 100), 288 (96), 253 (61), 225 (55), 190 (36)
3k	yellow	190–192	1616, 1511, 1349, 887	9.98 (d, 1 H, *J* = 7.2), 8.32 (d, 2 H, *J* = 8.6), 7.62 (d, 2 H, *J* = 8.6), 7.55 (d, 1 H, *J* = 8.8), 7.22–6.93 (m, 2 H), 6.50 (s, 1 H), 2.05 (s, 3 H)	280 (M^+, 100), 265 (89), 219 (69), 190 (31)
3l	yellow	105–107	1609, 1497, 1251, 1033, 836	9.98 (d, 1 H, *J* = 7.2), 7.50 (d, 1 H, *J* = 8.8), 7.33 (d, 2 H, *J* = 8.5), 7.18 (t, 1 H, *J* = 7.7), 6.98 (d, 2 H, *J* = 6.9), 6.89 (m, 1 H), 6.47 (s, 1 H), 3.88 (s, 3 H), 2.10 (s, 3 H)	265 (M^+, 12), 250 (97), 207 (31), 191 (28), 178 (100)
3m	yellow	oil	1680, 1602, 1504, 1230, 759	9.54 (d, 1 H, *J* = 6.9), 7.50–7.27 (m, 6 H), 7.05 (m, 1 H), 6.82 (m, 1 H), 6.51 (s, 1 H), 4.21 (q, 2 H, *J* = 6.9), 1.08 (t, 3 H, *J* = 6.9)	265 (M^+, 58), 193 (100), 192 (23)
3n	yellow	oil	1680, 1504, 1230, 751, 681	9.52 (d, 1 H, *J* = 6.9), 7.58–7.42 (m, 2 H), 7.33–7.28 (m, 3 H), 7.05 (t, 1 H, *J* = 6.9), 6.83 (t, 1 H, *J* = 6.9), 6.47 (s, 1 H), 4.10 (q, 2 H, *J* = 7.0), 0.94 (t, 3 H, *J* = 7.0)	301 (5), 299 (M^+, 15), 131 (100)
3o	yellow	52–54	1673, 1504, 1420, 1228, 836	9.52 (d, 1 H, *J* = 7.1), 7.48 (d, 1 H, *J* = 8.9), 7.42–7.34 (m, 4 H), 7.05 (m, 1 H), 6.82 (m, 1 H), 6.47 (s, 1 H), 4.20 (q, 2 H, *J* = 7.1), 1.11 (t, 3 H, *J* = 7.1)	301 (4), 299 (M^+, 11), 139 (100), 111 (37)
3p	yellow	78–80	1666, 1497, 1420, 829, 781	9.54 (d, 1 H, *J* = 7.0), 7.60 (d, 1 H, *J* = 2.0), 7.45 (d, 2 H, *J* = 8.4), 7.32 (m, 1 H), 7.07 (m, 1 H), 6.84 (t, 1 H, *J* = 6.9), 6.48 (s, 1 H), 4.22 (q, 2 H, *J* = 7.1), 1.15 (t, 3 H, *J* = 7.1)	337 (8), 335 (47), 333 (M^+, 73), 263 (63), 261 (100), 225 (37)

Table 3 (continued)

Product[a]	Color	mp (°C)	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	MS (70 eV) *m/z* (%)
3q	yellow	155–156	1680, 1595, 1511, 1342, 1229, 857	9.54 (d, 1 H, *J* = 7.2), 8.25 (d, 2 H, *J* = 8.8), 7.64 (d, 2 H, *J* = 8.8), 7.64 (d, 1 H, *J* = 8.8), 7.10 (m, 1 H), 6.89 (m, 1 H), 6.53 (s, 1 H), 4.21 (q, 2 H, *J* = 7.1), 1.09 (t, 3 H, *J* = 7.1)	310 (M^+, 58), 282 (22), 238 (100)
3r	yellow	99–101	1666, 1503, 1461, 830	9.52 (d, 1 H, *J* = 6.4), 7.44 (d, 3 H, *J* = 8.7), 7.02 (m, 1 H), 6.93 (d, 2 H, *J* = 8.7), 6.79 (m, 1 H), 6.47 (s, 1 H), 4.21 (q, 2 H, *J* = 7.1), 1.63 (s, 3 H), 1.13 (t, 3 H, *J* = 7.1)	295 (M^+, 91), 267 (23), 223 (100)
3s	orange	138–140	1595, 1511, 1342, 857, 730, 702	8.26 (d, 2 H, *J* = 8.7), 8.13 (d, 1 H, *J* = 7.0), 7.55 (d, 2 H, *J* = 8.7), 7.47 (d, 1 H, *J* = 8.9), 7.32–7.27 (m, 6 H), 6.83 (m, 1 H), 6.57 (t, 1 H, *J* = 6.6)	314 (M^+, 100), 268 (23)
3t	orange	149–150	1588, 1511, 1342, 857, 773	8.23 (d, 1 H, *J* = 7.1), 8.19 (d, 2 H, *J* = 5.4), 7.49–7.39 (m, 4 H), 7.23–7.20 (m, 4 H), 6.84 (m, 1 H), 6.60 (m, 1 H)	350 (37), 348 (100)
3u	orange	194–196	1595, 1511, 1342, 864, 857	8.28 (d, 2 H, *J* = 8.6), 8.09 (d, 1 H, *J* = 7.1), 7.53 (d, 2 H, *J* = 8.6), 7.45 (d, 1 H, *J* = 8.7), 7.24–7.16 (m, 5 H), 6.82 (m, 1 H), 6.56 (m, 1 H)	350 (34), 348 (M^+, 100), 302 (39)
3v	orange	226–228	1595, 1511, 1342, 829	8.31 (d, 2 H, *J* = 8.8), 8.07 (d, 1 H, *J* = 7.1), 7.56–7.30 (m, 6 H), 7.01 (m, 1 H), 6.70 (m, 1 H), 6.59 (m, 1 H)	386 (12), 384 (66), 382 (M^+, 100), 336 (31)

[a] Satisfactory elemental analyses obtained: C ± 0.28, H ± 0.30, N ± 0.29.
[b] Lit. mp 136–138 °C;[12] 137–137.5 °C.[17]

1-Unsubstituted 2-Arylindolizines 3a–v; General Procedure

A stirred suspension of 2-(2-arylethenyl)pyridinium salt **2** (10 mmol) and TPCD (6.08 g, 10 mmol) in toluene (100 mL) was treated dropwise with Et_3N (0.92 g, 10 mmol) at 80–90 °C. After 4 to 6 h (monitored by TLC), the solid was filtered off and washed with acetone (3 × 10 mL). The solvent was removed from the combined filtrates under vacuum to give the crude product **3**, which was purified by column chromatography [silica gel, 10% EtOAc in petroleum ether (bp 60–90 °C)].

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