

# A Convenient and Expedient Synthesis of 3-Aryl-2*H*-azirine-2-carboxaldehydes

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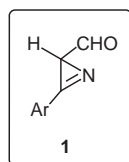
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**Abstract:** A new procedure for the synthesis of 3-aryl-2*H*-azirine-2-carboxaldehydes starting from cinnamyl alcohols is disclosed. This novel approach implies milder conditions and higher overall yields as compared to the previously reported methods. The key step, i.e. the formation of the azirine ring, involves the treatment of (Z)-3-aryl-3-azidoprop-2-en-1-ols with MnO<sub>2</sub>.

**Key words:** aldehydes, azides, heterocycles, oxidation, ring closure

Azirines bearing a carbonyl functionality at 2 position are valuable intermediates in heterocyclic chemistry, undergoing thermal and photochemical rearrangements to produce larger ring heterocycles. The scope of these ring expansion reactions, of interest not only from the synthetic but also from the mechanistic point of view, has been extensively investigated.<sup>1,2</sup> Several research groups have reported convenient routes to isoxazoles,<sup>3a,b</sup> oxazoles,<sup>3a,b</sup> pyrazoles,<sup>3a-c</sup> imidazoles,<sup>3a-c</sup> pyrroles<sup>3a-c</sup> and azepines<sup>3b,c</sup> based on the ring opening of either 2*H*-azirine-2-carboxaldehydes or 2-vinyl-2*H*-azirines and 2-aryliminomethyl-2*H*-azirines; the latter are obtained after derivatization of the corresponding 2*H*-azirine-2-carboxaldehydes **1** (Figure 1).



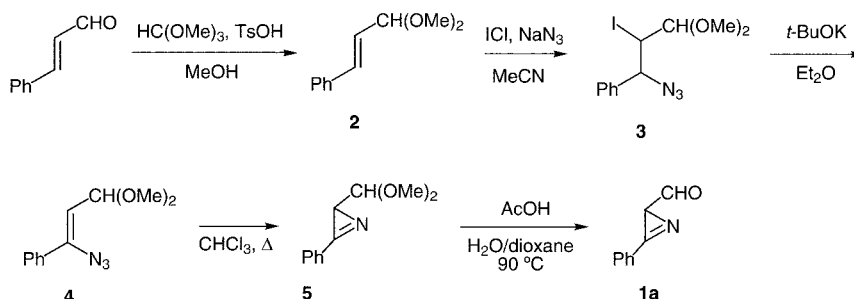
**Figure 1** Structure of 3-aryl-2*H*-azirine-2-carboxaldehydes

The role of 2*H*-azirine-2-carboxaldehydes as precursors of formyl-substituted (vinylimino)phosphoranes in the synthesis of nicotinates deserves consideration.<sup>4</sup> Likewise, a variety of transition metals are reactive toward these functionalized azirines effecting ring-opening processes to give isoxazoles, pyrazoles and pyrroles under exceedingly mild conditions.<sup>5</sup>

Amongst the procedures which have been reported for the synthesis of the most representative member of this series, i.e. 3-phenyl-2*H*-azirine-2-carboxaldehyde (**1a**), the one described by Padwa and co-workers is outstanding.<sup>6</sup> This method, the most widely used to date, is summarized in Scheme 1. The approach starts from cinnamaldehyde and consists in the addition of iodine azide to the dimethyl acetal **2** to give the iodoazide **3**, followed by dehydrohalogenation under basic conditions, thermolysis of the corresponding vinyl azide **4** and aqueous hydrolysis of the 3-phenyl-2*H*-azirine **5**. Following this sequence, the target 3-phenyl-2*H*-azirine-2-carboxaldehyde (**1a**) was obtained in 20% overall yield.

Much earlier, Isomura and co-workers had briefly reported<sup>7</sup> the synthesis of **1a** by thermal decomposition of a mixture of (*E*)- and (*Z*)-β-azidocinnamaldehyde in benzene at 50 °C followed by sublimation. Due to the synthetic versatility of 3-aryl-2*H*-azirine-2-carboxaldehydes **1**, short and efficient methods for their preparation are still in demand.

Here, we report a new synthetic route to compounds **1** which is an useful alternative to those described above, with similar overall yields and milder conditions for the key step, i.e. the formation of the azirine ring.



**Scheme 1** Established synthetic approach to 3-phenyl-2*H*-azirine-2-carboxaldehyde (**1a**)

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The synthetic scheme starts from the easily accessible cinnamyl alcohols **6** which were readily converted into the corresponding (Z)-3-aryl-3-azidoprop-2-en-1-ols **8** by a reported method (Scheme 2).<sup>8</sup> This approach involves bromination of **6** to give the *erythro*-2,3-dibromoprop-1-ols **7**. The intermediates **7** were further converted to the (Z)-3-azidoprop-2-en-1-ols **8** by treatment with NaN<sub>3</sub> in DMSO and subsequent dehydrobromination under basic conditions in a one-pot reaction (Scheme 2 and Table 1).

**Table 1** (Z)-3-Aryl-3-azidoprop-2-en-1-ols **8** from Cinnamyl Alcohols **6**

Entry	Compound	R	Yield (%) <sup>a</sup>
1	<b>8a</b>	Ph	57 <sup>b</sup>
2	<b>8b</b>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	30
3	<b>8c</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	51
4	<b>8d</b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	31

<sup>a</sup> Overall yield after chromatography.

<sup>b</sup> Ref.<sup>8</sup>

The key step involves the treatment of the azido alcohols **8** with MnO<sub>2</sub> at room temperature. Thus, when **8a** was allowed to react under these conditions, 3-phenyl-2*H*-azirine-2-carboxaldehyde (**1a**) was isolated in moderate yield (Scheme 2 and Table 2, entry 1). The (Z)-3-aryl-3-azidoprop-2-en-1-ols **8b–d** were also successfully converted into the corresponding 2*H*-azirine-2-carboxaldehydes **1b–d**, although they were obtained along with minor amounts of the isoxazoles **9**. Nevertheless, the respective azirines **1** and isoxazoles **9** could be readily separated by column chromatography (Scheme 2 and Table 2, entries 2–4).

The almost negligible amount of isoxazoles **9** might have formed by a ring-opening/ring-closure process of azirines **1b–d**. Such transformation has been reported to occur in the presence of light,<sup>1</sup> heat<sup>1,3</sup> or some oxidants.<sup>5</sup>

A comparison of the synthetic sequence shown in Scheme 1 for the preparation of **1a** and the new one here disclosed (Scheme 2) shows that although both start from easily available materials and the total yields are nearly comparable, the present sequence is shorter and requires

**Table 2** 3-Aryl-2*H*-azirine-2-carboxaldehydes **1** from Azido Alcohols **8**

Entry	Compound	R	<b>1</b> (%) <sup>a</sup>	<b>9</b> (%) <sup>a</sup>
1	<b>a</b>	Ph	55	— <sup>b</sup>
2	<b>b</b>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	52	9 <sup>c</sup>
3	<b>c</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	52	7 <sup>d,e</sup>
4	<b>d</b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	44	6 <sup>c,e</sup>

<sup>a</sup> After chromatography.

<sup>b</sup> Not detected.

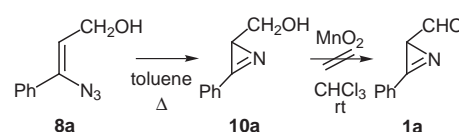
<sup>c</sup> Ref.<sup>9</sup>

<sup>d</sup> Ref.<sup>10</sup>

<sup>e</sup> Ref.<sup>11</sup>

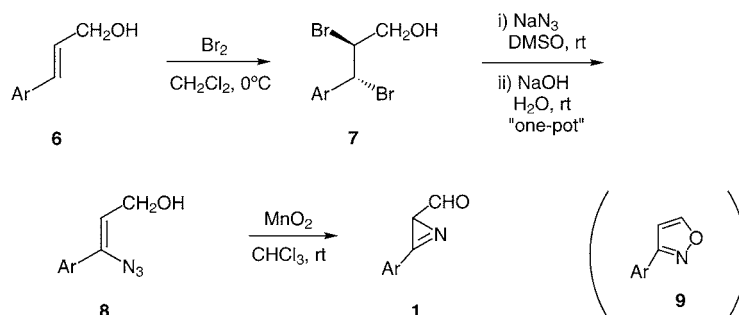
milder reaction conditions. For these reasons, we believe that the synthesis of **1** disclosed here may be considered as a suitable alternative to the ones previously described.

The transformation **8** → **1** came out as a surprise when we attempted the simple oxidation of the primary alcohol functionality of **8**. Thus, we decided to investigate the sequence of events in this step by means of 2-hydroxymethyl-3-phenyl-2*H*-azirine (**10a**) (Scheme 3), synthesized by thermolysis of the azido alcohol **8a**.<sup>8</sup> Further treatment of **10a** with MnO<sub>2</sub> at room temperature did not lead to the aldehyde **1a**, but left **10a** unaltered. This result suggests that the oxidation of the azido alcohol probably takes place previously to the formation of the three-membered ring.



**Scheme 3** Preparation of 2-hydroxymethyl-3-phenyl-2*H*-azirine (**10a**) and its treatment with MnO<sub>2</sub>

The role of the hydroxymethyl substituent in the cyclization process was further investigated by submitting  $\alpha$ -azidostyrene<sup>12</sup> to a similar treatment with MnO<sub>2</sub>, but the expected azirine **11a** was not detected at all and the starting material was isolated intact (Scheme 4). Thus, the presence of the hydroxymethyl functionality *cis* to the azido group in the starting alkene (which is presumably oxi-



**Scheme 2** New approach to 3-aryl-2*H*-azirine-2-carboxaldehydes **1**

dized in a first step) seems to be mandatory for the cyclization to take place.



**Scheme 4** Treatment of  $\alpha$ -azidostyrene with  $\text{MnO}_2$

In conclusion, we have developed a new approach to 3-aryl-2H-azirine-2-carboxaldehydes, highly valuable intermediates in organic synthesis, which compares favorably with methods previously reported.

$\text{MnO}_2$  was purchased from Aldrich (activated, 5 micron, ca. 85%) and was dried at 120 °C for 24–48 h before use. Melting points were taken on a Reichert apparatus and are not corrected. IR spectra were recorded on a FT-IR Nicolet Impact 400 IR spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker AC 200 ( $^1\text{H}$ : 200 MHz,  $^{13}\text{C}$ : 50 MHz) or Varian Unity-300 ( $^1\text{H}$ : 300 MHz,  $^{13}\text{C}$ : 75 MHz) spectrometer with TMS ( $\delta = 0.00$ ) for the  $^1\text{H}$  and the  $\text{CDCl}_3$  residual peak ( $\delta = 77.1$ ) for the  $^{13}\text{C}$  resonances as internal standards. Mass spectra were obtained using a Hewlett-Packard 5993C spectrometer (electron impact technique, 70 eV) and VG Analytical AUTOSPEC spectrometer (FAB<sup>+</sup> technique with an EBE configuration at a 8kV accelerating voltage, a FAB Cs gun operating at 25kV and 3-nitrobenzyl alcohol as a matrix). Elemental analyses were performed on a Carlo Erba EA 1108-Elemental analyzer.

#### (Z)-3-Aryl-3-azidoprop-2-en-1-ols **8**; General Procedure

A solution of  $\text{Br}_2$  (1.62 g, 10.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (60 mL) was added dropwise to a solution of the corresponding cinnamyl alcohol **6** (10.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (75 mL) at 0 °C, with stirring under  $\text{N}_2$ , at the rate that the color of  $\text{Br}_2$  faded continuously. The addition of  $\text{Br}_2$  requires about 1 h. The solution was stirred for 20 min more at 0 °C and then, poured into 150 mL of a 5% aq  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The organic layer was separated and the aqueous phase was extracted with EtOAc ( $3 \times 50$  mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), filtered, and then concentrated to give the corresponding erythro-3-aryl-2,3-dibromopropan-1-ol **7**, which was used in the next step without further purification. Thus, a solution of the dibromide **7** (9.3 mmol) in DMSO (10 mL) was added to a suspension of  $\text{NaN}_3$  (0.71 g, 11.0 mmol) in the same solvent (20 mL) at 0 °C under  $\text{N}_2$  and stirred for 24 h at r.t. At this time, a solution of NaOH (0.51 g, 12.8 mmol) in  $\text{H}_2\text{O}$  (10 mL) was added dropwise to the reaction mixture at 0 °C and stirred for 92 h at the same temperature. The mixture was poured into  $\text{H}_2\text{O}$  (50 mL) and the organic materials were extracted with EtOAc ( $3 \times 50$  mL). The combined extracts were washed with  $\text{H}_2\text{O}$  and brine, dried ( $\text{MgSO}_4$ ), filtered, and then concentrated to give a residue, which was purified by column chromatography eluting with EtOAc–hexanes, 1:3.

#### (Z)-3-Azido-3-phenylprop-2-en-1-ol (**8a**)<sup>8</sup>

Yield: 57% (Lit.<sup>8</sup> 57%); yellow oil.

IR (neat): 3327, 2113, 1650, 1492, 1025, 966, 711, 704  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 2.30$  (br s, 1 H), 4.35 (d, 2 H,  $J = 6.7$  Hz), 5.36 (t, 1 H,  $J = 6.7$  Hz), 7.35–7.40 (m, 5 H).

#### (Z)-3-Azido-3-(4-methylphenyl)prop-2-en-1-ol (**8b**)

Yield: 30%; mp 55–56 °C (colorless prisms from  $\text{Et}_2\text{O}$ – $n$ -pentane).

IR (nujol): 3224, 2113, 1648, 1507, 1025, 1016, 957, 789, 723, 647  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.90$  (t, 1 H,  $J = 5.0$  Hz), 2.38 (s, 3 H), 4.35 (m, 2 H), 5.33 (t, 1 H,  $J = 6.8$  Hz), 7.20–7.23 (m, 2 H), 7.26–7.29 (m, 2 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 21.3$ , 58.3, 117.6, 127.1, 129.5, 131.6, 139.3, 139.4.

EI-MS:  $m/z$  (%) = 161 ( $\text{M}^+ - 28$ , 11), 144 (73), 118 (100).

Anal. Calcd for  $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}$  (189.22): C, 63.48; H, 5.86; N, 22.21. Found: C, 63.21; H, 5.77; N, 22.18.

#### (Z)-3-Azido-3-(4-chlorophenyl)prop-2-en-1-ol (**8c**)

Yield: 51%; mp 53–56 °C (colorless prisms from  $n$ -hexane).

IR (nujol): 3314, 2113, 1645, 1491, 1099, 1014, 964, 844, 726, 641  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.86$  (br s, 1 H), 4.36 (d, 2 H,  $J = 6.6$  Hz), 5.37 (t, 1 H,  $J = 6.6$  Hz), 7.33 (d, 2 H,  $J = 8.6$  Hz), 7.40 (d, 2 H,  $J = 8.6$  Hz).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 58.2$ , 118.9, 128.5, 129.2, 132.9, 135.4, 138.2.

EI-MS:  $m/z$  (%) = 211 ( $[\text{M} + 2]^+$ , 2), 209 ( $\text{M}^+$ , 5), 140 (30), 138 (100).

Anal. Calcd for  $\text{C}_9\text{H}_8\text{ClN}_3\text{O}$  (209.63): C, 51.57; H, 3.85; N, 20.04. Found: C, 51.42; H, 3.75; N, 20.16.

#### (Z)-3-Azido-3-(4-bromophenyl)prop-2-en-1-ol (**8d**)

Yield: 31%; yellow oil.

IR (neat): 3429, 2110, 1648, 1487, 1079, 1015, 959, 831  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 2.09$  (br s, 1 H), 4.35 (d, 2 H,  $J = 6.8$  Hz), 5.37 (t, 1 H,  $J = 6.8$  Hz), 7.22–7.29 (m, 2 H), 7.52–7.58 (m, 2 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 58.1$ , 118.9, 123.5, 128.7, 132.1, 133.3, 138.1.

EI-MS:  $m/z$  (%) = 227 ( $[\text{M} + 2]^+ - 28$ , 8), 225 ( $\text{M}^+ - 28$ , 8), 210 (100), 208 (97).

Anal. Calcd for  $\text{C}_9\text{H}_8\text{BrN}_3\text{O}$  (254.09): C, 42.54; H, 3.17; N, 16.54. Found: C, 42.18; H, 3.06; N, 16.68.

#### 3-Aryl-2H-azirine-2-carboxaldehydes **1**; General Procedure

$\text{MnO}_2$  (2.00 g) was added to a solution of the corresponding (Z)-3-aryl-3-azidoprop-2-en-1-ol **8** (1.0 mmol) in  $\text{CHCl}_3$  (15 mL). The reaction mixture was stirred at r.t. until the total disappearance of the azidoalcohol **8** (TLC on silica gel plate; EtOAc–hexanes, 1:3) (5–16 h). The crude product was filtered through a pad of Celite and the residue was washed with  $\text{CHCl}_3$  ( $3 \times 10$  mL). The filtrate was concentrated to give an oily residue which was further purified by silica gel chromatography eluting with the appropriate mixture of solvents.

#### 3-Phenyl-2H-azirine-2-carboxaldehyde (**1a**)<sup>6</sup>

Eluent: EtOAc–hexanes, 1:3; yield: 55% (16 h reaction time); mp 49–50 °C (Lit.<sup>6</sup> mp 49–51 °C).

IR (nujol): 1775, 1704, 1121, 1102, 990, 766, 689  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 2.89$  (d, 1 H,  $J = 6.5$  Hz), 7.59–7.71 (m, 3 H), 7.90–7.94 (m, 2 H), 8.97 (d, 1 H,  $J = 6.5$  Hz).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 39.0$ , 122.6, 129.5, 130.6, 134.5, 159.4, 200.0.

#### 3-(4-Methylphenyl)-2H-azirine-2-carboxaldehyde (**1b**)

Eluent:  $\text{Et}_2\text{O}$ –hexanes, 1:9; yield: 52% (5 h reaction time); mp 31–32 °C (colorless prisms from  $\text{Et}_2\text{O}$ – $n$ -pentane at –40 °C).

IR (nujol): 1772, 1716, 1111, 1093, 966, 820, 765  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.49 (s, 3 H), 2.85 (d, 1 H,  $J$  = 6.8 Hz), 7.41–7.43 (m, 2 H), 7.79–7.81 (m, 2 H), 8.93 (d, 1 H,  $J$  = 6.8 Hz).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 22.0, 39.0, 119.8, 130.3, 130.7, 145.7, 158.9, 200.3.

FAB-MS:  $m/z$  (%) = 160 ( $[\text{M} + 1]^+$ , 100), 159 ( $\text{M}^+$ , 14).

Anal. Calcd for  $\text{C}_{10}\text{H}_9\text{NO}$  (159.19): C, 75.45; H, 5.70; N, 8.80. Found: C, 75.05; H, 5.72; N, 8.94.

### 3-(4-Chlorophenyl)-2H-azirine-2-carboxaldehyde (1c)

Eluent:  $\text{Et}_2\text{O}$ –hexanes, 1:9; yield: 52% (5 h reaction time); mp 88–89 °C (colorless prisms from  $\text{Et}_2\text{O}$ – $n$ -hexane).

IR (nujol): 1774, 1718, 1688, 1126, 1090, 1017, 991, 843, 824  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.90 (d, 1 H,  $J$  = 6.4 Hz), 7.61 (d, 2 H,  $J$  = 8.4 Hz), 7.85 (d, 2 H,  $J$  = 8.4 Hz), 8.98 (d, 1 H,  $J$  = 6.4 Hz).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 39.1, 121.2, 130.2, 131.8, 141.2, 158.8, 199.6.

EI-MS:  $m/z$  (%) = 181 ( $[\text{M} + 2]^+$ , 14), 179 ( $\text{M}^+$ , 50), 153 (27), 151 (89), 89 (100).

Anal. Calcd for  $\text{C}_9\text{H}_6\text{ClNO}$  (179.60): C, 60.19; H, 3.37; N, 7.80. Found: C, 60.35; H, 3.47; N, 7.63.

### 3-(4-Bromophenyl)-2H-azirine-2-carboxaldehyde (1d)

Eluent:  $\text{EtOAc}$ –hexanes, 1:9; yield: 44% (5 h reaction time); mp 109–110 °C (colorless prisms from  $\text{Et}_2\text{O}$ – $n$ -pentane).

IR (nujol): 1773, 1715, 1690, 1119, 1066, 1013, 988, 844, 816  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.90 (d, 1 H,  $J$  = 6.4 Hz), 7.77 (s, 4 H), 8.98 (d, 1 H,  $J$  = 6.4 Hz).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 39.0, 121.6, 129.8, 131.8, 133.1, 159.0, 199.6.

EI-MS:  $m/z$  (%) = 225 ( $[\text{M} + 2]^+$ , 81), 223 ( $\text{M}^+$ , 80), 197 (30), 195 (31), 89 (100).

Anal. Calcd for  $\text{C}_9\text{H}_6\text{BrNO}$  (224.06): C, 48.25; H, 2.70; N, 6.25. Found: C, 48.18; H, 2.35; N, 6.28.

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