Reactions of Azides with Electrophiles: New Methods for the Generation of Cationic 2-Azabutadienes. Synthesis of 1,2,3,4-Tetrahydroquinolines and 1,2-Dihydroquinolines via a Hetero Diels–Alder Reaction

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Abstract. Two methods for the generation of iminium ions of the type ArN+(X)=CHR (X = H or alkyl, R = H or alkyl) are reported: (1) the Bronsted-acid-promoted rearrangement of benzylic azides and (2) the intermolecular Schmidt reactions of azides XN3 (X = aliphatic) with benzylic carbocations derived from benzylic alcohols ArCH(R)OH. The iminium ions ArN+(X)=CHR behave as cationic 2-azabutadienes in the presence of alkenes and alkynes, producing 1,2,3,4-tetrahydroquinolines and 1,2-dihydroquinolines by a hetero Diels–Alder reaction.

INTRODUCTION
An increasingly popular route to 1,2,3,4-tetrahydroquinolines 5 is the [4+2] cycloaddition of 2-azabutadienes 4 with alkenes (Scheme 1).1-13 Alkynes also may be used as dienophiles, producing 1,2-dihydroquinolines, but this reaction is rare.14 Cycloadditions typically require a cationic 2-azabutadiene 4, where X = H, alkyl or aryl (i.e., iminium ions), or a Lewis acid. The mechanism is probably a stepwise one.5,15 Three methods are available for the generation of the cationic intermediates 4: the condensation of arylamines with carbonyl compounds, especially formaldehyde and other aldehydes, in the presence of a proton source and a dienophile (pathway a);2,6,9,12 treatment of a preformed imine with a protic or Lewis acid (pathway b);3,8,10,13 and the ionization of a leaving group LG (e.g., benzotriazolyl,4 phenylthio,16 sulfonyl,11 or methoxy,7 pathway c). Each method has its merits and shortcomings, but there are a few general problems with the available technology. First, cycloadditions of 4 are most commonly observed with R1 = H or aryl; examples where R1 = alkyl are rare.4b,13 Second, pathway a may suffer from competition with a double cycloaddition, where the initial product 5 condenses with more aldehyde (especially formaldehyde) to generate another cationic 2-azabutadiene, which then participates in a second aza Diels–Alder reaction.6b,17 Third, cycloadditions leading to N-substi-
tuted tetrahydroquinolines (5, X = alkyl or aryl) are less common, usually requiring pathway c.\textsuperscript{4,7,11,16} Finally, as stated above, alkynes are rarely used as the dienophile.\textsuperscript{14}

We wish to report two azide-based routes to cationic 2-azabutadienes 4 for use in tetrahydroquinoline synthesis, namely the acid-promoted decomposition of azides 6 involving rearrangement of the aminodiazonium ions 7 (eq 1),\textsuperscript{18} and the Schmidt reaction of azides with carbocations 8, involving rearrangement of the aminodiazonium ions 9 (eq 2). These methods extend the scope of the basic cycloaddition approach to tetrahydro- and dihydroquinolines by addressing the problems outlined above.

\begin{equation}
\begin{array}{c}
\text{Scheme 2}
\end{array}
\end{equation}

**RESULTS AND DISCUSSION**

We recently reported both the intra- and intermolecular Schmidt reaction of aliphatic azides with carbocations, a rearrangement process which produces synthetically useful iminium ions (e.g., eq 2).\textsuperscript{19,20} While exploring the scope of this method, an attempt to use benzyl azide to capture cyclopentyl cation gave, rather than the expected intermolecular Schmidt reaction product N-benzylpiperidine 11 after hydride reduction of the iminium ion 10, the known tetrahydroquinoline 14 2\textsuperscript{1} in good yield (Scheme 2). Apparently, an acid-promoted rearrangement of benzyl azide to the iminium ion 12 had occurred, as in eq 1. This cationic 2-azabutadiene then participated in a [4+2] cycloaddition with cyclopentene to produce 13, which aromatized to 14 by proton loss. The Bronsted- or Lewis-acid-catalyzed decomposition of aliphatic azides (including benzyl azide) to imines and/or iminium ions, originally studied by Curtius but sometimes attributed to Schmidt, is well known.\textsuperscript{22}

Given the successful generation and cycloaddition of the cationic 2-azabutadiene 12 using the azide decomposition method (Scheme 2), we set out to explore the scope of this reaction. The generation of 12 in the presence of a variety of alkenes resulted in good yields of tetrahydroquinolines (Table 1). Both electron-rich (entries 2,4,5) and simple unactivated alkenes (entries 1,3,6) were effective dienophiles. Alkynes, rarely used in such cycloadditions,\textsuperscript{14} were found to be useful dienophiles, producing the dihydroquinolines 20 and 21 (entries 7,8). The acid-promoted rearrangement of (1-azidoethyl)benzene was also attempted (entries 9-12), presumably producing a substituted 2-azadiene 4, where X = H and R\textsubscript{1} = CH\textsubscript{3}. Indeed, successful results were obtained with styrene (entry 9) and N-vinylpyrrolidin-2-one (entry 11). The rarity of cycloadditions using cationic 2-azadienes bearing an alkyl group (i.e., 4 where R\textsubscript{1} = alkyl) makes these examples particularly important. Note that 1-hexene failed to participate in a similar cycloaddition (entry 10). Phenylacetylene (entry 12) led to an excellent yield of the quinoline 25, presumably due to air oxidation of the initially formed dihydroquinoline during isolation and purification. It is worth noting that the yields of the transformations shown in Table 1 are ultimately limited by the amount of aryl migration in the rearrangement of 7 to 4a (eq 1). That is, the migration of hydrogen or R\textsubscript{1} to nitrogen will not produce an iminium ion which is viable in the cycloaddition reaction. Given that benzyl azide is known to rearrange by all three pathways upon protonation,\textsuperscript{23,a,b} it is remarkable that the yields shown in Table 1, all based upon the azide as the limiting reagent, are as high as they are.

We realized that our work on the intermolecular Schmidt reaction of azides with carbocations (eq 2)\textsuperscript{19} also produced cationic 2-azabutadienes 4, and thus we were interested in exploring tetrahydroquinoline synthesis using this route. We have reported that the action of triflic acid or SnCl\textsubscript{4} on benzylic alcohols in the presence of various aliphatic azides resulted in the formation of iminium ions 4, although other iminium ions were also produced by the migration of hydrogen or R\textsubscript{1}.\textsuperscript{19,23} Table 2 shows the result of carrying out such reactions.
Table 2. Cycloaddition of 2-azabutadienes derived from the Schmidt reaction of benzylic alcohols with aliphatic azides

<table>
<thead>
<tr>
<th>Entry</th>
<th>Azide</th>
<th>Dienophile</th>
<th>Product (% yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph—N₃</td>
<td></td>
<td>14 (71)&lt;sup&gt;a,b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>Ph—N₃</td>
<td>Ph—</td>
<td>15 R = Ph (72)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>Ph—N₃</td>
<td>n-Bu—</td>
<td>16 R = n-Bu (58)</td>
</tr>
<tr>
<td>4</td>
<td>Ph—N₃</td>
<td></td>
<td>17 R = N[(CH₂)₂CO] (76)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>Ph—N₃</td>
<td></td>
<td>18 (43)&lt;sup&gt;a,b&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>Ph—N₃</td>
<td></td>
<td>19 (55)</td>
</tr>
<tr>
<td>7</td>
<td>Ph—N₃</td>
<td>Ph—</td>
<td>20 R = Ph (78)</td>
</tr>
<tr>
<td>8</td>
<td>Ph—N₃</td>
<td>n-Bu—</td>
<td>21 R = n-Bu (68)</td>
</tr>
<tr>
<td>9</td>
<td>Ph—N₃</td>
<td>Ph—</td>
<td>22 R = Ph (58)&lt;sup&gt;a,b&lt;/sup&gt;</td>
</tr>
<tr>
<td>10</td>
<td>Ph—N₃</td>
<td>n-Bu—</td>
<td>23 R = n-Bu (0)</td>
</tr>
<tr>
<td>11</td>
<td>Ph—N₃</td>
<td></td>
<td>24 R = N[(CH₂)₂CO] (74)&lt;sup&gt;a,b&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>Ph—N₃</td>
<td></td>
<td>25 (91)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Using triflic acid. <sup>b</sup>Using tin tetrachloride. <sup>c</sup>Yields are lower, since only the iminium ion resulting from aryl migration participates in the cycloaddition.<sup>1c,23</sup> 3:7:1 cis:trans, not separated. 3:1 cis:trans, not separated.

EXPERIMENTAL

(3aR*,9bS*)-2,3,3a,4,5,9b-Hexahydro-1H-cyclopenta[c]quinoline (14)<sup>23</sup>

Triflic acid (250 mL, 424 mg, 2.83 mmol) was added to a solution of benzyl azide (310 mg, 2.33 mmol) and cyclopentene (1.00 g, 14.68 mmol) in CH₂Cl₂ (15 mL) at 0 °C. After stirring for 10 min, NaBH₄ (530 mg, 14.00 mmol) in methanol (10 mL) was added at 0 °C. After stirring at room temperature overnight, 15% aqueous NaOH (40 mL) was added and the reaction mixture was extracted with ether (3 × 30 mL). The combined organic phases were washed with brine (40 mL), then dried (MgSO₄) and concentrated. Chromatography (1:16 ether/hex) gave 288 mg (71%) of the title compound, R<sub>f</sub> = 0.24. ¹H NMR (CDCl₃, 360 MHz) δ 7.08 (d, J = 7.4 Hz, 1 H), 6.96 (t, J = 7.7 Hz, 1 H), 6.67 (t, J = 7.3 Hz, 1 H), 6.52 (d, J = 7.9 Hz, 1 H), 3.81 (br s, 1 H), 3.08 (dd, J = 4.8, 11.0 Hz, 1 H), 2.97 (q, J = 8.3 Hz, 1 H), 2.77 (t, J = 10.4 Hz, 1 H), 2.40–2.26 (m, 1 H), 2.18–2.12 (m, 1 H), 1.99–1.91 (m, 1 H), 1.70–1.66 (m, 1 H), 1.63–1.49 (m, 2 H), 1.45–1.42 (m, 1 H); ¹³C NMR (CDCl₃, 90 MHz, JMOD) δ 144.8 (s), 129.8 (+), 126.3 (–), 126.1 (+), 117.6 (+), 114.5 (+), 44.4 (–), 40.6 (+), 36.2 (+), 35.3 (–), 29.3 (–), 23.5 (–); IR (neat) 3388 (br m), 1606 (s), 1584 (m), 1496 (s), 1362 (m), 1265 (m).
1075 (w), 747 (s) cm\(^{-1}\); MS (EI, 70 eV) \(m/z\) (rel int) 173 (M\(^+\), 93.6), 157 (5.3), 144 (34.4), 130 (100), 117 (13.4), 106 (9.4), 91 (7.9), 77 (14.7), 65 (5.8), 51 (5.6), 39 (6.9); HRMS (EI, 70 eV) calcd for C\(_{12}\)H\(_{17}\)N, 173.1204, found 173.1199. Anal. Calcd for C\(_{12}\)H\(_{17}\)N: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.12; H, 8.72; N, 8.28.

[4+2] Cycloaddition reactions of cationic 2-azabutadienes derived from the acid-promoted decomposition of azides. General procedure A

Triflic acid (1.2 equiv) was added to a solution of the desired benzylic azide (2.00 mmol) in CH\(_2\)Cl\(_2\) or benzene (8 mL) at 0 °C. After warming to room temperature over 10 min, the dienophile (in excess) was added at either 0 °C or room temperature. After stirring for the indicated amount of time at either room temperature or reflux, triethylamine (2 mL) was added and the reaction mixture was concentrated in vacuo to give the crude product, which was purified by flash chromatography on silica gel.

4-Phenyl-1,2,3,4-tetrahydroquinoline (15)\(^{24}\)

Prepared from benzyl azide (266 mg, 2.00 mmol), triflic acid (200 mL, 339 mg, 2.26 mmol), and styrene (0.50 mL, 455 mg, 4.37 mmol) in benzene (10 mL) at room temperature for 1 h according to general procedure A. Chromatography (1:7 ether/hex) gave 303 mg (72%) of the title compound as a clear oil, \(R_f = 0.30\) (1:7 ether/hex). \(^1\)H NMR (CDCl\(_3\), 360 MHz) \(\delta\) 7.37–7.33 (m, 2 H), 7.29–7.26 (m, 1 H), 7.22–7.19 (m, 2 H), 7.09–7.01 (m, 1 H), 6.83–6.80 (m, 1 H), 6.65–6.59 (m, 2 H), 4.20 (t, \(J = 6.1\) Hz, 1 H), 3.70 (br s, 1 H), 3.34–3.28 (m, 2 H), 2.27–2.24 (m, 1 H), 2.13–2.10 (m, 1 H); \(^13\)C NMR (CDCl\(_3\), 90 MHz) \(\delta\) 146.6, 144.9, 130.4, 128.6, 128.2, 127.2, 126.0, 123.3, 116.9, 114.1, 42.7, 39.1, 31.0; IR (neat) 3410 (s), 1606 (s), 1503 (s), 1314 (s), 1285 (s), 1083 (s), 745 (s); MS (EI, 70 eV) \(m/z\) (rel int) 209 (M\(^+\), 100), 194 (22.5), 180 (5.9), 165 (3.0), 150 (2.0), 145 (4.5), 130 (100), 117 (7.7), 103 (5.6), 84 (45.5), 77 (10.5), 45 (11.8); HRMS calcd for C\(_{13}\)H\(_{16}\)N\(_2\)O, 216.1266, found 216.1264. These data are consistent with those reported by Katritzky et al.\(^{25}\)

(4R*,10B*)-10b-Hexahydro-2H-pyrralo[3,2-c] quinoline (18)\(^{8}\)

Prepared from benzyl azide (266 mg, 2.00 mmol), triflic acid (200 mL, 339 mg, 2.26 mmol), and dihydropyran (0.50 mL, 461 mg, 5.48 mmol) in benzene (8 mL) at room temperature overnight according to general procedure A. Chromatography (1:2 ether/hex) gave 162 mg (43%) of the title compound as a clear oil, \(R_f = 0.34\). \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 7.26–7.20 (m, 1 H), 7.11–7.05 (m, 1 H), 6.70–6.66 (m, 1 H), 6.52–6.49 (m, 1 H), 4.47 (d, \(J = 3.0\) Hz, 1 H), 4.02–3.97 (m, 2 H), 3.74–3.66 (m, 1 H), 3.55 (t, \(J = 10.9\) Hz, 1 H), 3.02 (dd, \(J = 10.0\), 2.8 Hz, 1 H), 2.12–2.06 (m, 1 H), 1.95–1.72 (m, 3 H), 1.52–1.45 (m, 1 H); \(^13\)C NMR (CDCl\(_3\), JMOD, 75 MHz) \(\delta\) 144.8 (–), 130.5 (+), 128.7 (+), 120.7 (–), 117.0 (+), 114.2 (+), 73.6 (+), 66.8 (–), 42.0 (–), 32.5 (+), 25.4 (–); IR (neat) 3360 (m), 1611 (s), 1500 (s), 1377 (m), 1305 (s), 1083 (s), 1065 (s), 909 (m), 746 (s) cm\(^{-1}\); MS (CI with NH\(_3\)) \(m/z\) (rel int) 190 (M\(^+\)H\(^+\)), 100, 179 (1.9), 158 (1.3), 144 (3.3), 130 (33.3), 94 (22.2); HRMS (CI with NH\(_3\)) calcd for C\(_{16}\)H\(_{18}\)NO\(_2\) 190.1232, found 190.1237. These data are consistent with the limited data reported by Kametani et al.\(^{8}\)

5,6,6a,7,8,9,10,10a-Octahydro-7,10-methanophenanthenidine (19)\(^{26}\)

Prepared from benzyl azide (266 mg, 2.00 mmol), triflic acid (200 mL, 339 mg, 2.26 mmol), and norbornylene (450 mg, 4.78 mmol) in CH\(_2\)Cl\(_2\) (8 mL) at room temperature for 6 h and reflux overnight according to general procedure A. Chromatography (1:2 ether/hex) gave 218 mg (55%) of the title compound as a clear oil, \(R_f = 0.35\). \(^1\)H NMR (CDCl\(_3\), 360 MHz) \(\delta\) 7.76–7.23 (m, 1 H), 7.06–7.01 (m, 1 H), 6.84–6.80 (m, 1 H), 6.62–6.59 (m, 1 H), 3.59 (br s, 1 H), 3.23 (dd, \(J = 6.1\), 6.0 Hz, 1 H), 2.92 (dd, \(J = 6.5, 6.4\) Hz, 1 H), 2.74 (d, \(J = 8.8\) Hz, 1 H), 2.49 (d, \(J = 3.8\) Hz, 1 H), 2.22–2.13 (m, 2 H), 1.79–1.56 (m, 3 H), 1.53–1.34 (m, 2 H), 1.10–0.06 (m, 1 H); \(^13\)C

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NMR (CDCl₃, JMOD, 90 MHz) δ 147.2 (-), 129.2 (+), 127.9 (-), 125.8 (+), 118.8 (-), 115.1 (+), 46.2 (-), 45.5 (+), 44.0 (+), 43.7 (+), 42.2 (+), 34.4 (-), 30.1 (-), 29.2 (-); IR (neat) 3369 (m), 1605 (s), 1498 (s), 1481 (s), 1361 (m), 1296 (s), 46.2 (-), 45.5 (+), 44.0 (+), 43.7 (+), 42.2 (+), 34.4 (-), 30.1 (-), 29.2 (-); MS (EI, 70 eV) m/z (rel int) 199 (M⁺, 92.8), 170 (7.5), 156 (12.9), 143 (8.0), 130 (100), 118 (32.5), 1.6 (28.2), 91 (8.8), 77 (14.6), 39 (7.8); HRMS calcd for C₁₀H₁₇N₁⁺ 199.1361, found 199.1348.

4-Phenyl-1,2-dihydroquinoline (20)
Prepared from benzyl azide (266 mg, 2.00 mmol), triflic acid (200 mL, 339 mg, 2.26 mmol), and phenylacetylene (0.50 mL, 465 mg, 4.55 mmol) in CH₂Cl₂ (8 mL) at room temperature overnight according to general procedure A. Chromatography (1:2 ether/hex) gave 323 mg (78%) of the title compound as a clear oil, Rf = 0.32. IH NMR (CDCl₃, 360 MHz) δ 7.09 (d, J = 7.6 Hz, 1 H), 6.98 (dt, J = 1.3, 7.8 Hz, 1 H), 6.67 (t, J = 8.6 Hz, 1 H), 6.52 (dd, J = 1.2, 7.9 Hz, 1 H), 5.70 (t, J = 4.2 Hz, 1 H), 4.22 (d, J = 4.2 Hz, 2 H), 3.81 (br s, 1 H); 13C NMR (CDCl₃, 90 MHz) δ 145.5, 139.6, 138.4, 128.7, 128.6, 128.2, 127.3, 126.1, 122.3, 119.0, 117.8, 113.3, 43.9; IR (neat) 3391 (br s), 1602 (s), 1492 (s), 1306 (s), 1222 (s), 1140 (s), 935 (m) cm⁻¹. MS (EI, 70 eV) m/z 206.0972.
Triflic acid (1.1 equiv) or tin tetrachloride (1.0 M solution in CH₂Cl₂, 2.0 equiv) was added to a solution of the desired alcohol (2.00 mmol) and n-butylazide⁶ (in excess) in CH₂Cl₂ or benzene at 0 °C. After stirring for 10 min at 0 °C, the dienophile was added. After stirring at either room temperature or reflux, 15% aqueous NaOH (50 mL) was added and the mixture was extracted with ether (3 x 40 mL). The combined organic phases were washed with brine (2 x 40 mL), dried (Na₂SO₄) and concentrated to give the crude product, which was purified by flash chromatography on silica gel.

1-n-Butyl-4-phenyl-6-methoxy-1,2,3,4-tetrahydroquinoline (26)

Prepared from 4-methoxybenzyl alcohol (553 mg, 4.00 mmol), triflic acid (350 mL, 949 mg, 3.96 mmol), n-butylazide⁶ (793 mg, 8.00 mmol), and styrene (230 mL, 209 mg, 2.01 mmol, added at 0 °C) in CH₂Cl₂ (15 mL) at room temperature overnight according to general procedure B. Chromatography (1:7 ether/hex) gave 392 mg (66%) of the title compound as a clear oil, Rf = 0.47. ¹H NMR (CDCl₃, 300 MHz) δ 7.33 (dt, J = 8.1, 1.2 Hz, 2 H), 7.27–7.24 (m, 1 H), 7.18–7.15 (m, 2 H), 6.77 (dd, J = 8.9, 3.0 Hz, 1 H), 6.68 (d, J = 8.9 Hz, 1 H), 6.44 (d, J = 2.9 Hz, 1 H), 4.15 (t, J = 5.9 Hz, 1 H), 3.68 (s, 3 H), 3.30 (q, J = 8.1 Hz, 2 H), 3.21 (dt, J = 6.0, 1.6 Hz, 2 H), 2.35–2.23 (m, 1 H), 2.16–2.04 (m, 1 H), 1.72–1.58 (2 H, 1.50–1.38 (2 H, 1.02 (t, J = 7.3 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 150.5, 146.3, 140.4, 128.1, 126.0, 125.5, 116.2, 113.4, 112.0, 55.8, 51.9, 46.3, 43.9, 31.1, 28.5, 20.6, 14.0; IR (neat) 1601 (m), 1506 (s), 1460 (m), 1421 (s), 1285 (s), 1170 (m), 1055 (s), 997 (m), 947 (s), 880 (m), 803 (m) cm⁻¹; MS (EI, 70 eV) m/z (rel int) 295 (M⁺, 55.1), 280 (4.5), 225 (100), 228 (5.4), 197 (3.3), 160 (5.6), 146 (2.7), 117 (4.0), 91 (14.2), 44 (21.2); HRMS calcd for C₁₇H₂₆N₂O₂ 295.1936, found 295.1942.

1-n-Butyl-4-(2-oxopyrrolidin-1-yl)-6-methoxy-1,2,3,4-tetrahydroquinoline (27)

Prepared from 4-methoxybenzyl alcohol (553 mg, 4.00 mmol), triflic acid (400 mL, 678 mg, 4.52 mmol), n-butylazide⁶ (793 mg, 8.00 mmol), and 1-vinyl-2-pyrrolidinone (200 mL, 208 mg, 1.87 mmol, added at 0 °C) in CH₂Cl₂ (20 mL) at room temperature overnight according to general procedure B. Chromatography (ether) gave 436 mg (77%) of the title compound as a clear oil, Rf = 0.29. ¹H NMR (CDCl₃, 300 MHz) δ 6.70 (dd, J = 8.9, 0.3 Hz, 1 H), 6.54 (d, J = 8.9 Hz, 1 H), 6.45 (d, J = 3.0 Hz, 1 H), 5.34 (dd, J = 8.9, 5.9 Hz, 1 H), 3.69 (s, 3 H), 3.34–3.23 (m, 1 H), 3.21–3.09 (m, 5 H), 2.46 (t, J = 8.1 Hz, 2 H), 2.09–2.05 (m, 1 H), 2.03–1.93 (m, 3 H), 1.54–1.47 (m, 2 H), 1.41–1.30 (m, 2 H), 0.93 (t, J = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz, JMOD) δ 175.0 (–), 150.8 (–), 140.8 (–), 120.0 (–), 114.3 (+), 113.6 (+), 112.7 (+), 55.9 (+), 51.8 (+), 48.3 (+), 47.3 (+), 43.7 (+), 31.4 (–), 28.2 (–), 26.9 (–), 20.4 (–), 18.3 (–), 13.9 (+); IR (neat) 1685 (s), 1506 (s), 1460 (m), 1421 (s), 1285 (s), 1170 (m), 1055 (m), 1040 (m), 805 (m) cm⁻¹; MS (EI, 70 eV) m/z (rel int) 302 (M⁺, 100), 259 (34.5), 216 (69.3), 205 (16.0), 174 (67.6), 160 (26.2), 138 (10.7), 114 (43.8), 98 (20.8), 41 (25.2); HRMS calcd for C₁₇H₂₆N₂O₂ 302.1949, found 302.01.0.
CONCLUSION
The two methods reported herein for the generation of iminium ions of the type ArN(+)X=CHR (X = H or alkyl, R = H or alkyl), namely the Bronsted-acid-promoted rearrangement of benzylidic azides and the intermolecular Schmidt reactions of aliphatic azides with benzylidic carbocations, provide alternatives to the existing methods for the generation of such cationic 2-azabutadienes. Hetero Diels–Alder reactions of these cationic dienes proceed efficiently, producing 1,2,3,4-tetrahydroquinolines and 1,2-dihydroquinolines. Attractive features of this methodology include the ability to use alkynes as dienophiles, and to produce N(1)- and C(2)-alkyl hydroquinolines. Also, in contrast to current hydrogenated quinoline derivatives described herein successfully address some of the problems associated with current routes, thus enhancing the generality of the hetero Diels–Alder approach to these compounds.

REFERENCES AND NOTES
(17) This process may be desirable, such as in syntheses of the julolidines.
(18) In related work, Aubé has found that benzylidic azides rearrange to N-aryl iminium ions in the presence of Lewis acids, and that these cationic 2-azabutadienes may participate in Mannich-type chemistry: J. Aubé (University of Kansas), personal communication.
(23) For example, the Schmidt reaction of p-methoxybenzyl alcohol and α-methyl-p-methoxybenzyl alcohol led to...
a mixture of iminium ions resulting from both aryl and hydrogen migration:18

\[
\begin{align*}
\text{For } R^1 &= \text{H: aryl:H migration} = 1:1.9 \\
\text{For } R^1 &= \text{Me: aryl:H:methyl migration} = 12.3:2.5:1
\end{align*}
\]

(27) For the preparation and spectral data of a similar compound, 4-methyltetrahydroquinoline, see: Kano, S.; Tanaka, Y.; Hibino, S. *Heterocycles* 1980, 14, 39–41.