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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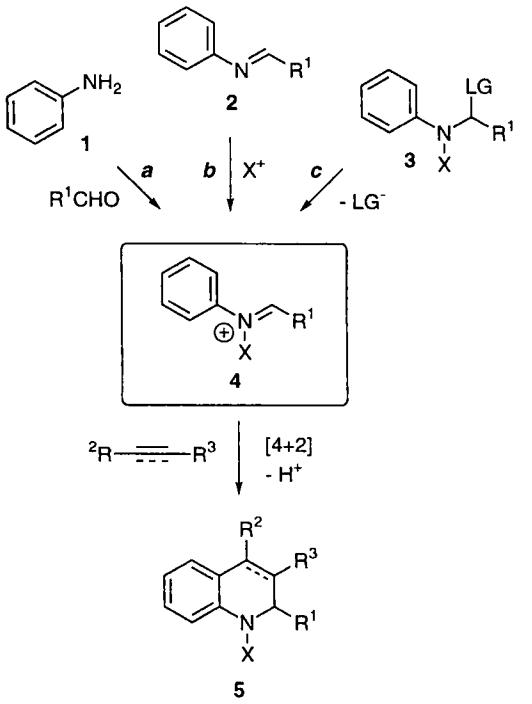
Abstract. Two methods for the generation of iminium ions of the type $ArN^+(X)=CHR$ (X = H or alkyl, R = H or alkyl) are reported: (1) the Bronsted-acid-promoted rearrangement of benzylic azides and (2) the intermolecular Schmidt reactions of azides XN_3 (X = aliphatic) with benzylic carbocations derived 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.[2,8,15] 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 R^1 = H or aryl; examples where R^1 = 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.[6,9,17] Third, cycloadditions leading to *N*-substi-



Scheme 1. Generation and cycloaddition of 2-azabutadienes

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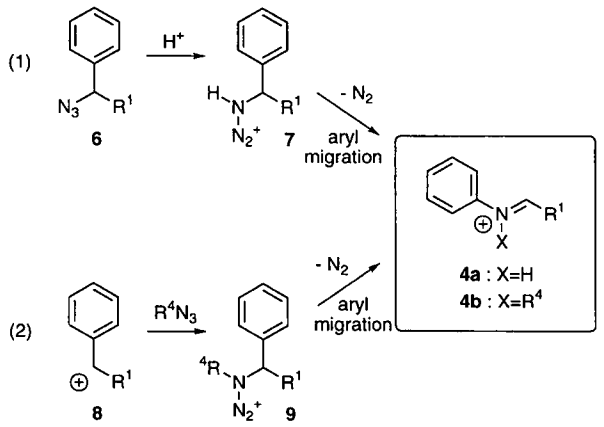
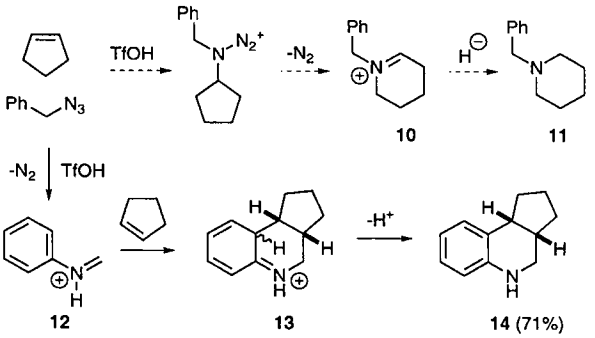
tuted tetrahydroquinolines (**5**, X = alkyl or aryl) are less common, usually requiring pathway *c*.[4,7,11,16] Finally, as stated above, alkynes are rarely used as the dienophile.[14] We wish to report two azide-based routes to cationic 2-azabutadienes **4** for use in tetrahydroquinoline synthesis, namely the acid-promoted decomposition of azides **6** involving rearrangement of the aminodiazonium ions **7** (eq 1),[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.





Scheme 2

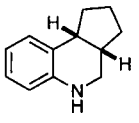
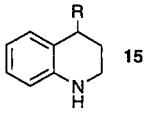
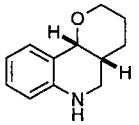
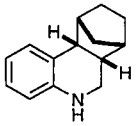
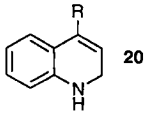
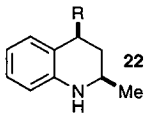
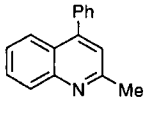
RESULTS AND DISCUSSION

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).[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**[21] 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.[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,[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 $R^1 = CH_3$. Indeed, successful results were obtained with styrene (entry 9) and *N*-vinylpyrrolidin-2-one (entry 11). The rarity[4b,13] of cycloadditions using cationic 2-azadienes bearing an alkyl group (i.e., **4** where R^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^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,[22a,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)[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 $SnCl_4$ 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^1.[19,23] Table 2 shows the result of carrying out such reactions

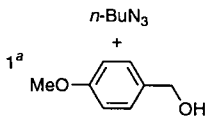
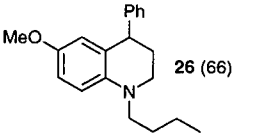
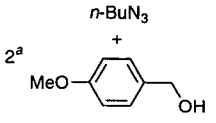
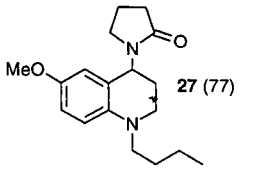
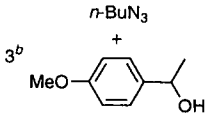
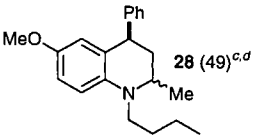
Table 1. Cycloaddition of 2-azabutadienes derived from the acid-promoted rearrangement of azides

Entry	Azide	Dienophile	Product (% yield)
1			 **14** (71)[a,b]
2			 **15** R = Ph (72)[b]
3			**16** R = *n*-Bu (56)
4			**17** R = N[$(CH_2)_3$CO] (76)[b]
5			 **18** (43)[a,b]
6			 **19** (55)
7			 **20** R = Ph (78)
8			**21** R = *n*-Bu (66)
9			 **22** R = Ph (58)[a,b]
10			**23** R = *n*-Bu (0)
11			**24** R = N[$(CH_2)_3$CO] (74)[a,b]
12			 **25** (91)[b]

[a]One diastereomer within the detection limits of high-field ^{1}H NMR. [b]Known compounds: **14**,[21] **15**,[24] **17**,[4b,25] **18**,[8] **22**,[28] **24**,[4b] **25**.[30]

in the presence of dienophiles. The tetrahydroquinolines **26–29** were formed in moderate to good yield based on the amount of the alcohol. Based on the actual proportion of aryl migration, these yields would be higher.[23] The Schmidt route to cationic 2-azabutadienes, besides providing a completely new way to access these systems, provides for the incorporation of aliphatic substituents at N(1) and C(2) of the tetrahydroquinolines.

Table 2. Cycloaddition of 2-azabutadienes derived from the Schmidt reaction of benzylic alcohols with aliphatic azides

Entry	Azide/ Alcohol	Dienophile	Product (% yield)
1[a]			 **26** (66)
2[a]			 **27** (77)
3[b]			 **28** (49)[c,d]
4[a]			**29** (36)[c,e]

[a]Using trifilic acid. [b]Using tin tetrachloride. [c]Yields are lower, since only the iminium ion resulting from aryl migration participates in the cycloaddition.[19c,23] [d]3.7:1 *cis:trans*, not separated. [e]3:1 *cis:trans*, not separated.

EXPERIMENTAL

(3aR,9bS*)-2,3,3a,4,5,9b-Hexahydro-1*H*-cyclopenta[c] quinoline (14)*[21]

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 CH_2Cl_2 (15 mL) at 0 °C. After stirring for 10 min, $NaBH_4$ (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 ($MgSO_4$) and concentrated. Chromatography (1:16 ether/hex) gave 288 mg (71%) of the title compound, R_f = 0.24. ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 90 MHz, JMOD) δ 144.8 (–), 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), 1298 (s), 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 $C_{12}H_{15}N$ 173.1204, found 173.1199. Anal. Calcd for $C_{12}H_{15}N$ 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_2Cl_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 1h 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). ^1H NMR ($CDCl_3$, 360 MHz) δ 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) δ 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 (m), 1155 (s), 1030 (m), 919 (m), 746 (s) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 209 (M^+, 100), 194 (22.5), 180 (14.3), 165 (7.9), 152 (5.6), 130 (35.2), 103 (4.7), 91 (15.9), 77 (8.8), 49 (6.0); HRMS calcd for $C_{15}H_{15}N$ 209.1204, found 209.1195.

*4-n-Butyl-1,2,3,4-tetrahydroquinoline (**16**)*

Triflic acid (200 mL, 339 mg, 2.26 mmol) was added to a solution of benzyl azide (266 mg, 2.00 mmol) and 1-hexene (3.0 mL, 2.02 g, 23.99 mmol) in benzene (8 mL) at 0 °C, and the resulting mixture was allowed to warm to room temperature. After 1h, saturated aqueous $NaHCO_3$ (10 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 ($MgSO_4$) and concentrated. Chromatography (1:7 ether/hex) gave 210 mg (56%) of the title compound as a clear oil, R_f = 0.35 (1:2 ether/hex). ^1H NMR ($CDCl_3$, 360 MHz) δ 7.04 (d, *J* = 7.2 Hz, 1 H), 6.98 (dt, *J* = 1.5, 7.6 Hz, 1 H), 6.64 (dt, *J* = 1.2, 7.4 Hz, 1 H), 6.49 (dd, *J* = 1.2, 8.0 Hz, 1 H), 3.70 (br s, 1 H), 3.38–3.24 (m, 2 H), 2.75 (dt, *J* = 5.0, 9.8 Hz, 1 H), 1.96–1.90 (m, 1 H), 1.86–1.75 (m, 1 H), 1.74–1.63 (m, 1 H), 1.60–1.50 (m, 1 H), 1.49–1.33 (m, 4 H), 0.95 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 144.1, 129.1, 126.7, 125.7, 116.6, 114.1, 38.4, 36.4, 35.4, 29.2, 26.1, 22.9, 14.1; IR (neat) 3409 (s), 1606 (s), 1499 (s), 1358 (m), 1313 (s), 1269 (m), 1099 (m), 745 (s) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 189 (M^+, 56.0), 160 (1.6), 144 (3.7), 132 (100), 117 (14.6), 84 (18.0), 77 (7.8), 49 (16.5); HRMS calcd for $C_{13}H_{19}N$ 189.1517, found 189.1519.

*4-(2-Oxopyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (**17**)*[4b,25]

Prepared from benzyl azide (266 mg, 2.00 mmol), triflic acid (200 mL, 339 mg, 2.26 mmol), and 1-vinyl-2-pyrrolidinone (250 mL, 260 mg, 2.34 mmol, added at –78 °C) in CH_2Cl_2 (8 mL) at room temperature overnight according to general procedure A. Chromatography (ether) gave 330 mg (76%) of the title compound as a clear oil, R_f = 0.19. ^1H NMR ($CDCl_3$, 360 MHz) δ 7.01–6.97 (m, 1 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 6.63–6.59 (m, 1 H), 6.50–6.48 (m, 1 H), 5.39 (dd, *J* = 8.8, 6.0 Hz, 1 H), 3.97 (br s, 1 H), 3.41–3.34 (m, 1 H), 3.31–3.19 (m, 2 H), 3.14–3.08 (m, 1 H), 2.46 (dd, *J* = 8.2, 6.2 Hz, 2 H), 2.08–1.90 (m, 4 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 175.4, 145.7, 128.2, 127.8, 118.6, 117.4, 114.7, 47.4, 43.5, 40.1, 31.4, 26.5, 18.2; IR (neat) 3340 (m), 1670 (s), 1607 (s), 1498 (s), 1421 (s), 1317 (s), 1285 (s) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 216 (M^+, 32.6), 205 (9.9), 187 (5.9), 145 (5.5), 130 (100), 117 (7.7), 103 (5.6), 84 (45.5), 77 (10.5), 47 (11.8); HRMS calcd for $C_{13}H_{16}N_2O$ 216.1263, found 216.1266. These data are consistent with those reported by Katritzky et al.[4b,25]

(4aR,10bR*)-3,4,4a,5,6,10b-Hexahydro-2H-pyrano[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. ^1H NMR ($CDCl_3$, 300 MHz) δ 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) δ 144.8 (–), 130.5 (+), 128.7 (+), 120.7 (–), 117.0 (+), 114.2 (+), 73.6 (+), 66.8 (–), 42.0 (–), 32.5 (+), 25.4 (–), 22.9 (–); IR (neat) 3360 (m), 1611 (s), 1500 (s), 1377 (m), 1305 (m), 1083 (s), 1065 (s), 909 (m), 746 (s) cm^{-1}; MS (CI with NH_3) *m/z* (rel int) 190 ($[M+H]^+$, 100), 170 (1.9), 158 (1.3), 144 (3.3), 130 (33.3), 94 (22.2); HRMS (CI with NH_3) calcd for $C_{12}H_{15}NOH$ 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-methanophenanthridine (**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_2Cl_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. ^1H NMR ($CDCl_3$, 360 MHz) δ 7.26–7.23 (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), 1.10–1.06 (m, 1 H); ^{13}C

NMR ($CDCl_3$, 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), 1259 (s), 1124 (s), 751 (s) cm^{-1}; 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 $C_{14}H_{17}N$ 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 CH_2Cl_2 (8 mL) at room temperature overnight according to general procedure A. Chromatography (1:2 ether/hex) gave 323 mg (78%) of the title compoound as a clear oil, R_f = 0.45. ^1H NMR ($CDCl_3$, 360 MHz) δ 7.41–33 (m, 5 H), 7.02 (dt, *J* = 1.5, 7.6 Hz, 1 H), 6.87 (dd, *J* = 1.3, 7.7 Hz, 1 H), 6.60 (dt, *J* = 1.2, 7.4 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); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 145.5, 139.6, 138.4, 128.7, 128.6, 128.2, 127.3, 126.1, 122.3, 120.9, 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* (rel int) 205 (M^+, 100), 176 (19.8), 151 (8.1), 131 (2.5), 102 (15.4), 88 (13.0), 69 (8.2), 51 (4.4); HRMS (CI with NH_3) calcd for $C_{15}H_{11}NH$ 206.0970, found 206.0972.

*4-Butyl-1,2-dihydroquinoline (**21**)*[27]

Prepared from benzyl azide (266 mg, 2.00 mmol), triflic acid (200 mL, 339 mg, 2.26 mmol), and 1-hexyne (1.00 mL, 715 mg, 8.70 mmol) in benzene (8 mL) at room temperature for 180 min according to general procedure A. Chromatography (1:2 ether/hex) gave 245 mg (66%) of the title compound as a clear oil, R_f = 0.32. ^1H NMR ($CDCl_3$, 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), 6.43 (d, *J* = 7.9 Hz, 1 H), 5.52 (t, *J* = 4.0 Hz, 1 H), 4.09 (d, *J* = 4.0 Hz, 2 H), 3.68 (br s, 1 H), 2.37 (t, *J* = 7.2 Hz, 2 H), 1.57–1.51 (m, 2 H), 1.48–1.40 (m, 2 H), 0.98 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 145.4, 135.2, 128.1, 123.4, 122.0, 118.1, 117.6, 112.9, 42.8, 31.6, 30.2, 22.6, 13.9; IR (neat) 3392 (s), 1650 (s), 1603 (s), 1499 (s), 1464 (s), 1307 (s), 1137 (s), 1012 (m), 745 (s) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 186 ([M-H]$^+$, 57.0), 170 (5.0), 156 (14.0), 143 (100), 130 (24.4), 115 (21.4), 84 (44.4), 77 (9.2), 63 (6.0), 49 (20.3); HRMS calcd for $C_{13}H_{17}N$ 187.1361, found 187.1345.

(2R,4S*)-2-Methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (**22**)*[28]

Prepared from (1-azidoethyl)benzene[29] (600 mg, 4.08 mmol), triflic acid (400 mL, 678 mg, 4.52 mmol), and styrene (1.00 mL, 909 mg, 8.73 mmol, added at 0 °C) in CH_2Cl_2 (20 mL) at reflux overnight according to general procedure A. Chromatography (1:7 ether/hex) gave 529 mg (58%) of the title compound as a clear oil, R_f = 0.30. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.44–7.36 (m, 2 H), 7.34–7.30 (m, 3 H), 7.09–7.03 (m, 1 H), 6.71–6.67 (m, 1 H), 6.63–6.58 (m, 2 H), 4.23 (dd, *J* = 12.3, 5.5 Hz, 1 H), 3.85 (br s, 1 H), 3.73–3.63 (m, 1 H), 2.22 (ddd, *J* = 12.8, 7.9, 2.4 Hz, 1 H), 1.93 (q, *J* = 12.8 Hz, 1 H), 1.31 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, JMOD) δ 145.7 (–), 145.1 (–), 129.5 (+), 128.5 (+), 128.3 (+), 126.9 (+), 126.2 (+), 124.7 (–), 117.1 (+), 113.9 (+), 47.7 (+), 44.6 (+), 41.3 (–), 22.5 (+); IR (neat) 3389 (br s), 1604 (s), 1486 (s), 1312 (s), 1165 (s), 1063 (m), 749 (s), 701 (s) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 223 (M^+, 77.2), 208 (100), 193 (9.2), 180 (8.6), 165 (9.4), 144 (8.8), 130 (24.6), 115 (9.1), 91 (35.8), 77 (14.6); HRMS calcd for $C_{16}H_{17}N$ 223.1361, found 223.1358. Previous reports of this compound do not include spectral data.[28] Katritzky et al.[4b] have reported a similar compound, using proton NMR to determine its stereochemistry. We were able to use their method for the assignment of the stereochemistry of **22**.

(2R,4S*)-2-Methyl-4-(2-oxopyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (**24**)*[4b]

Prepared from (1-azidoethyl)benzene[29] (600 mg, 4.08 mmol), triflic acid (400 mL, 678 mg, 4.52 mmol), and 1-vinyl-2-pyrrolidinone (500 mL, 520 mg, 4.68 mmol, added at 0 °C) in CH_2Cl_2 (16 mL) at 0 °C for 1h and room temperature for 180 min according to general procedure A. Chromatography (ether) gave 656 mg (74%) of the title compound as a clear oil, R_f = 0.23. ^1H NMR ($CDCl_3$, 360 MHz) δ 6.98 (t, *J* = 7.8 Hz, 1 H), 6.80 (d, *J* = 7.7 Hz, 1 H), 6.63 (t, *J* = 7.4 Hz, 1 H), 6.49 (d, *J* = 8.0 Hz, 1 H), 5.54 (dd, *J* = 12.1, 6.1 Hz, 1 H), 3.76 (br s, 1 H), 3.55 (dt, *J* = 10.6, 5.2 Hz, 1 H), 3.25–3.18 (m, 1 H), 3.15–3.09 (m, 1 H), 2.51–2.45 (m, 2 H), 2.03–1.90 (m, 3 H), 1.70 (q, *J* = 11.7 Hz, 1 H), 1.20 (d, *J* = 6.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 175.6, 145.8, 128.0, 126.7, 118.8, 117.7, 114.6, 47.9, 46.8, 42.1, 34.0, 31.4, 22.2, 18.1; IR (neat) 3330 (br s), 1672 (s), 1606 (s), 1491 (s), 1411 (s), 1313 (s), 1270, 1168 (s), 911 (m), 750 (s) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 230 (M^+, 25.1), 201 (8.6), 159 (4.1), 144 (67.0), 130 (100), 117 (8.4), 103 (8.9), 77 (14.8), 41 (6.5); HRMS calcd for $C_{14}H_{18}N_2O$ 230.1419, found 230.1418. These data were consistent with those reported by Katritzky et al.[4b]

*2-Methyl-4-phenylquinoline (**25**)*[30]

Prepared from (1-azidoethyl)benzene[29] (600 mg, 4.08 mmol), triflic acid (400 mL, 678 mg, 4.52 mmol), and phenylacetylene (2.00 mL, 1.86 g, 18.22 mmol, added at 0 °C) in benzene (45 mL) at room temperature overnight according to general procedure A. Chromatography (1:2 ether/hex) gave 814 mg (91%) of the title compound as a clear oil, R_f = 0.27. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.10 (d, *J* = 8.4 Hz, 1 H), 7.86 (dd, *J* = 8.4, 1.1 Hz, 1 H), 7.68 (dt, *J* ; = 6.9, 1.4 Hz, 1 H), 7.52–7.46 (m, 5 H), 7.42 (dt, *J* = 6.9, 1.1 Hz, 1 H), 7.23 (s, 1 H), 2.78 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.2, 148.4, 138.1, 129.3, 129.0, 128.9, 128.7, 128.3, 128.1, 125.5, 125.4, 125.0, 122.0, 25.2; IR (neat) 1592 (s), 1498 (s), 1407 (s), 1195 (m), 1030 (m), 877 (m), 744 (s) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 219 (M^+, 100), 204 (10.3), 176 (6.5), 151 (3.2), 131 (7.6), 106 (10.6), 84 (11.9), 77 (11.5), 44 (32.5); HRMS calcd for $C_{16}H_{13}N$ 219.1048, found 219.1050.

[4+2] Cycloaddition reactions of cationic 2-azabutadienes derived from the Schmidt reaction of azides with benzylic alcohols. General procedure B

Triflic acid (1.1 equiv) or tin tetrachloride (1.0 M solution in CH_2Cl_2, 2.0 equiv) was added to a solution of the desired alcohol (2.00 mmol) and *n*-butylazide[31] (in excess) in CH_2Cl_2 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 × 40 mL). The combined organic phases were washed with brine (2 × 40 mL), dried (Na_2SO_4) 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, 594 mg, 3.96 mmol), *n*-butylazide[31] (793 mg, 8.00 mmol), and styrene (230 mL, 209 mg, 2.01 mmol, added at 0 °C) in CH_2Cl_2 (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, R_f = 0.47. ^{1}H NMR ($CDCl_3$, 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 (m, 2 H), 1.50–1.38 (m, 2 H), 1.02 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.5, 146.3, 140.4, 128.6, 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), 1465 (s), 1288 (s), 1248 (s), 1162 (s), 1051 (s), 806 (m), 701 (s) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 295 (M^+, 55.1), 280 (4.5), 252 (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 $C_{20}H_{25}NO$ 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*-butylazide[31] (793 mg, 8.00 mmol), and 1-vinyl-2-pyrrolidinone (200 mL, 208 mg, 1.87 mmol, added at 0 °C) in CH_2Cl_2 (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, R_f = 0.29. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.70 (dd, *J* = 8.9, 3.0 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); ^{13}C NMR ($CDCl_3$, 75 MHz, JMOD) δ 175.0 (–), 150.8 (–), 140.8 (–), 120.6 (–), 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 $C_{18}H_{26}N_2O_2$ 302.1994, found 302.2001.

(2R,4R*)-1-*n*-Butyl-2-methyl-4-phenyl-1,2,3,4-tetrahydroquinoline and (2R*,4S*)-1-*n*-Butyl-2-methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (28)*

Prepared from phenethyl alcohol (620 mg, 5.07 mmol), tin tetrachloride (10.00 mL, 1.0 M solution in CH_2Cl_2, 10.00 mmol), *n*-butylazide[31] (3.00 g, 30.26 mmol), and styrene (1.60 mL, 1454 mg, 13.97 mmol, added at 0 °C) in benzene (30 mL) at reflux overnight according to general procedure B. Chromatography (5% ether in hexanes) gave 694 mg (49%) of the title compound as a clear oil, R_f = 0.50, which proved to be an inseparable 3:1 mixture of *cis* and *trans* diastereomers by ^{1}H NMR. Data for the mixture of diastereomers: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35–7.26 (m, 2 H), 7.24–7.13 (m, 2 H), 7.08–7.00 (m, 1 H), 6.68–6.58 (m, 2 H), 6.55–6.42 (m, 2 H), 4.03 (dd, *J* = 11.5, 4.6 Hz, 1 H), 3.58–3.49 (m, 1 H), 3.46–3.31 (m, 1 H), 3.25–3.05 (m, 1 H), 2.23–2.14 (m, 1 H), 2.10–1.95 (m, 1 H), 1.71–1.50 (m, 2 H), 1.45–1.30 (m, 2 H), 1.20 (d, *J* = 6.2 Hz, 3 H), 1.96 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.3, 146.0, 145.1, 129.5, 129.1, 128.7, 128.6, 128.3, 128.2, 127.2, 127.1, 126.2, 126.1, 124.7, 117.0, 115.8, 114.8, 112.6, 112.2, 110.7, 52.7, 51.3, 49.3, 48.4, 43.9, 43.7, 41.2, 40.3, 37.9, 31.8, 29.7, 21.6, 20.5, 19.7, 14.0, 13.9; IR (neat) 1599 (s), 1494 (s), 1331 (s), 1184 (s), 1067 (m), 909 (w), 745 (s) 700 (s) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 279 (M^+, 41.6), 264 (52.7), 236 (100), 206 (9.6), 194 (14.9), 165 (10.3), 144 (9.5), 130 (12.2), 105 (6.3), 91 (26.3); HRMS calcd for $C_{20}H_{25}N$ 279.1987, found 279.1960.

(2R,4R*)-1-*n*-Butyl-2-methyl-4-(2-oxopyrrolidin-1-yl)-6-methoxy-1,2,3,4-tetrahydroquinoline and (2R*,4S*)-1-*n*-Butyl-2-methyl-4-(2-oxopyrrolidin-1-yl)-6-methoxy-1,2,3,4-tetrahydroquinoline (29)*

Prepared from 4-methoxyphenethyl alcohol (609 mg, 4.00 mmol), triflic acid (400 mL, 678 mg, 4.52 mmol), *n*-butylazide[31] (2.38 g, 24.01 mmol), and 1-vinyl-2-pyrrolidinone (1.28 mL, 1.33 g, 11.98 mmol, added at 0 °C) in CH_2Cl_2 (30 mL) at room temperature overnight according to general procedure B. Chromatography (ether) gave 456 mg (36%) of the title compound as a clear oil, R_f = 0.29, which was shown to be an inseparable 3.7:1 mixture of *cis* and *trans* diastereomers by ^{1}H NMR. Data for the mixture of diastereomers: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.69 (dd, *J* = 2.9, 0.7 Hz, 0.3 H), 6.66 (dd, *J* = 2.9, 0.6 Hz, 0.7 H), 6.62 (s, 0.7 H), 6.59 (s, 0.3 H), 6.47–6.44 (m, 0.3 H), 6.35 (dd, *J* = 2.7, 1.0 Hz, 0.7 H), 5.42 (dd, *J* = 11.7, 5.8 Hz, 1 H), 3.67 (s, 3 H), 3.46–3.34 (m, 1 H), 3.30–3.15 (m, 3 H), 3.14–2.98 (m, 1 H), 2.50–2.41 (m, 2 H), 2.05–1.95 (m, 2 H), 1.93–1.75 (m, 2 H), 1.56–1.42 (m, 2 H), 1.38–1.28 (m, 2 H), 1.24 (d, *J* = 6.2 Hz, 2.1 H), 1.15 (d, *J* = 6.6 Hz, 0.7 H), 0.95–0.89 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 175.3, 175.2, 151.3, 150.6, 141.6, 139.5, 122.7, 119.9, 114.4, 114.2, 113.7, 113.1, 112.4, 111.9, 56.0, 55.8, 51.4, 49.9, 48.4, 48.2, 45.3, 42.9, 42.4, 35.8, 31.9, 31.5, 31.4, 30.0, 29.0, 21.5, 20.4, 18.4, 17.8, 14.0, 13.9; IR (neat) 1682 (s), 1498 (s), 1422 (s), 1375 (s), 1287 (s), 1205 (s), 1041 (s), 803 (m) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 316 (M^+, 100), 273 (35.3), 259 (8.1), 230 (22.0), 216 (94.3), 188 (64.3), 174 (27.3), 160 (23.8), 98 (13.2), 41 (13.3); HRMS calcd for $C_{19}H_{28}N_2O_2$ 316.2151, found 316.2161.

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 benzylic azides and the intermolecular Schmidt reactions of aliphatic azides with benzylic 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 methodology involving the condensation of anilines with aldehydes, double-cycloadditions are not observed. Overall, the azide-based routes to partially 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.

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(17) This process may be desirable, such as in syntheses of the julolidines.[4c,7]

(18) In related work, Aubé has found that benzylic 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.

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(20) For leading references on Aubé's related work on the intra- and intermolecular Schmidt reactions of azides with Lewis-acid-activated carbonyl compounds, see: (a) Aubé, J.; Milligan, G.L. *J. Am. Chem. Soc.* **1991**, *113*, 8965–8966. (b) Milligan, G.L.; Mossman, C.J.; Aubé, J. *J. Am. Chem. Soc.* **1995**, *117*, 10449–10459.

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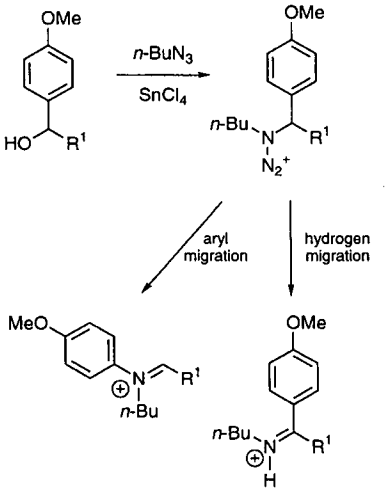
(23) For example, the Schmidt reaction of *p*-methoxybenzyl alcohol and α-methyl-*p*-methoxybenzyl alcohol led to

a mixture of iminium ions resulting from both aryl and hydrogen migration:[19c]



For R^1=H: aryl:H migration = 1:1.9
For R^1=Me: aryl:H:methyl migration = 12.3:2.5:1

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