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One-pot synthesis of azacyclodiynes by reaction of α,ω-diacetylenes with 1,5,3-dioxazepanes using copper-containing catalysts

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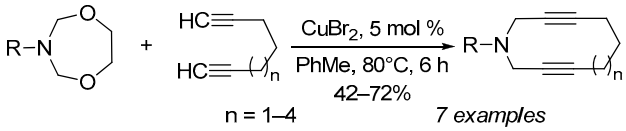


An effective method has been developed for the synthesis of cyclic propargylamines by aminomethylation of α,ω-diacetylenes with *N*-alkyl-substituted 1,5,3-dioxazepanes in the presence of copper-containing catalysts.

Keywords: *N*-alkyl-substituted 1,5,3-dioxazepanes, α,ω-diacetylenes, cyclic propargylamines, aminomethylation, catalysis.

Azacycloalkynes have been previously obtained in reactions of primary amines with α,ω-dihaloalkadiynes,[1] by intramolecular cyclization of diacetylenic *gem*-amino ethers under high dilution conditions,[2] by a three-component cyclocondensation of terminal alkadiynes, aldehydes, and amines (A^3-coupling) in the presence of CuCl catalyst,[3] as well as by aminomethylation of α,ω-diacetylenes by using *N*,*N*-bis(ethoxymethyl)amines in the presence of $CuBr_2$ catalyst.[4]

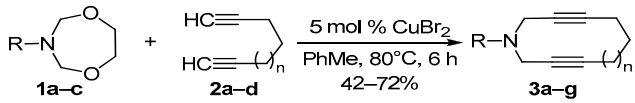
It has been previously reported that 1,5,3-dioxazepanes[5] can be effectively used as Mannich bases in aminomethylation reactions of β-keto esters[6] and cyclopentanone.[7] In the current work, we present data about the synthesis of azacycloalkadiynes by catalytic cycloaminomethylation of α,ω-diacetylenes using *N*-substituted 1,5,3-dioxazepanes.

The interest toward azacycloalkadiynes is motivated by their applications in organic synthesis, for example, in thermal intramolecular cyclization reactions of 1,6-diazacyclodeca-3,8-diynes[8] or 1-thia-6-azacyclodeca-3,8-diynes.[9]

While continuing our exploration of aminomethylation reactions of terminal acetylenes using 1,5,3-dioxazepanes,[10] as well as for the purpose of developing an effective method for the synthesis of azacyclodiynes, we studied the reaction of α,ω-diacetylenes with *N*-substituted 1,5,3-dioxazepanes **1a**–**c** in the presence of copper-containing catalysts. The selection of catalysts on the basis of copper compounds was justified by their high activity in reactions between terminal acetylenes and *N*,*N*-bis(ethoxymethyl)amines.[4]

By using the model reaction of 3-butyl-1,5,3-dioxazepane (**1b**) with 1,7-octadiyne (**2b**), we screened catalysts that were either pure copper compounds (CuCl (5% yield of the product), CuBr (16%), CuI (25%), $CuCl_2$ (36%), $CuBr_2$ (65%), $CuSO_4$ (7%)) or immobilized copper catalysts on solid supports ($CuCl_2 \cdot 2H_2O$–γ-Al_2O_3 (25% yield of the product), $CuBr_2$–γ-Al_2O_3 (23%), $CuBr_2$–microSiO_2 (7%), $CuBr_2$–mesoSiO_2 (16%), $CuBr_2$–macroSiO_2 (15%), $CuBr_2$–ASM-40 (14%), $CuBr_2$–HY-BS (10%)). The highest yield (~65%) of 1-butyl-1-azacycloundeca-3,9-diyne (**3d**) was achieved by using 5 mol % of $CuBr_2$ catalyst at 80°C over 6 h in toluene under argon atmosphere. The reaction of α,ω-alkadiynes **2a**–**d** with 1,5,3-dioxazepanes **1a**–**c** under these conditions led to 1-alkyl-1-azacycloalkadiynes **3a**–**g** in 42–72% yields (Scheme 1). The spectral characteristics of compounds **3c**,**d**,**e**,**g** matched the literature data.[4]

Scheme 1



	2a n = 1	2b n = 2	2c n = 3	2d n = 4
1a R = *n*-Pr			**3a**	**3b**
1b R = *n*-Bu	**3c**	**3d**		**3e**
1c R = *t*-Bu	**3f**	**3g**		

Cycloalkyl(cyclopropyl,cyclopentyl,cyclohexyl)- and aryl-substituted 1,5,3-dioxazepanes did not react with α,ω-diacetylenes under the aforementioned conditions, because the indicated 1,5,3-dioxazepanes were converted to 1,3,5-triazines under the reaction conditions developed during our study. The α,ω-diacetylenes containing a heteroatom – (di(propyn-2-yl)ether and *N*,*N*-di(propyn-2-yl)amine) showed low activity in the reaction with alkyl-substituted 1,5,3-dioxazepanes, probably due to conformational rigidity caused by the effects of lone electron pairs of the heteroatom on the structure of α,ω-diacetylene.

Thus, we have developed a new one-pot method for the synthesis of azacyclodiynes by cycloaminomethylation of α,ω-diacetylenes using *N*-substituted 1,5,3-dioxazepanes in the presence of $CuBr_2$ catalyst.

Experimental

IR spectra were recorded on a Bruker Vertex 70v spectrometer for samples in the form of thin films. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 (400 and 100 MHz, respectively) and Bruker Ascend 500 (500 and 125 MHz, respectively) spectrometers in $CDCl_3$. Homonuclear (COSY) and heteronuclear (^1H–^{13}C HSQC, ^1H–^{13}C HMBC) two-dimensional NMR experiments for compounds **3a**–**e** were performed on a Bruker Avance 500 spectrometer. The chemical shifts were determined relative to solvent signals (δ_H 7.28 ppm and δ_C 77.1 ppm, respectively). GC/MS analyses were performed on a Shimadzu GC 2010 chromatograph with a Shimadzu GCMS-QP2010 Ultra mass selective detector. The gas chromatograph was equipped with a Supelco 5ms capillary column (60 m × 0.25 mm × 0.25 μm), carrier gas – helium, injector temperature 260°C, interface temperature 260°C, ion source temperature 200°C, EI ionization (70 eV). The content of C, H, and N was determined with a Carlo Erba 1106 CHN-analyzer. Gas chromatography was performed on a Shimadzu GC-9A with a flame ionization detector, using SE-30 stationary phase (5%) on a Chromaton N-AW-HMDS support, 2000 × 3 mm packed steel column, temperature program 50–280°C, 8°C/min, the carrier gas was helium. Thin-layer chromatography was performed on Sorbfil PTSKh-AF-A plates, with visualization in iodine vapor. Individual compounds were isolated by chromatographic separation on KSK silica gel (50–160 μm). The eluent used for column chromatography is indicated for each compound.

The starting α,ω-diacetylenes **2a**–**d** with ≥98% assay were commercially available from Acros Organics and were used without additional purification, while 1,5,3-dioxazepanes **1a**–**c** were synthesized according to published procedures.[5] Copper salts (CuBr, CuI, $CuCl_2$, $CuBr_2$, $CuCl_2{\cdot}2H_2O$, $CuSO_4$, and $Cu(CH_3CO_2)_2$) with ≥99% assay were commercially available from Acros Organics. The catalysts on solid support were obtained by coating copper salts on solid carriers. The procedure involved treatment of γ-Al_2O_3, micro-meso, meso, and macroporous silica gels, as well as acidic amorphous alumosilicate and micro-mesomacroporous zeolite HY (HY-BS) with the aforementioned copper salts as solutions in alcohol or ether, followed by drying at 110°C according to a published method.[11] All samples contained 10–12 mass % of the respective copper salts.

Synthesis of 1-alkyl-1-azacycloalkadiynes 3a–g (General method). A Schlenk vessel was charged under argon atmosphere with the appropriate 1,5,3-dioxazepane **1a**–**c** (1 mmol), toluene (3 ml), α,ω-diacetylene **2a**–**d** (1 mmol), and $CuBr_2$ (0.01 g, 0.05 mmol). The reaction mixture was stirred at 80°C for 6 h and filtered through a layer of silica gel; the solvent was evaporated on a rotary evaporator. The product was isolated by column chromatography.

1-Propyl-1-azacyclododeca-3,10-diyne (3a). Yield 0.085 g (42%), yellow oil. R_f 0.53 (hexane–dichloromethane, 1:1). IR spectrum, ν, cm^{-1}: 1140 (C–N), 1432 (CH_3), 1457 (CH_2), 2258 (C≡C), 2860 (CH_2), 2934 (CH_3). ^1H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 0.93 (3H, t, *J* = 7.5, CH_3); 1.48–1.53 (8H, m, $(C{\equiv}CCH_2C\underline{H}_2)_2C\underline{H}_2$, $C\underline{H}_2CH_3$); 2.21–2.23 (4H, m, $N(CH_2C{\equiv}CC\underline{H}_2)_2$); 2.45 (2H, t, *J* = 7.5, $CH_3CH_2C\underline{H}_2N$); 3.38 (4H, s, $N(C\underline{H}_2C{\equiv}C)_2$). ^{13}C NMR spectrum (125 MHz), δ, ppm: 12.0 (CH_3); 18.7 ($2C{\equiv}C\underline{C}H_2$); 20.7 ($\underline{C}H_2CH_3$); 28.3 ($(C{\equiv}CCH_2\underline{C}H_2)_2\underline{C}H_2$); 28.5 ($2C{\equiv}CCH_2\underline{C}H_2$); 42.5 ($N(\underline{C}H_2C{\equiv}C)_2$); 54.9 ($CH_2\underline{C}H_2N$); 75.1 ($N(CH_2\underline{C}{\equiv}C)_2$); 84.8 ($N(CH_2C{\equiv}\underline{C})_2$). Mass spectrum, *m*/*z* (I_{rel}, %): 203 $[M]^+$ (11), 188 $[M–CH_3]^+$ (3), 174 $[M–CH_2CH_3]^+$ (100), 160 $[M–CH_3(CH_2)_2]^+$ (9), 132 $[M–N(CH_2)_3CH_3]^+$ (7). Found, %: C 82.76; H 10.34; N 6.91. $C_{14}H_{21}N$. Calculated, %: C 82.70; H 10.41; N 6.89.

1-Propyl-1-azacyclotrideca-3,11-diyne (3b). Yield 0.132 g (60%), yellow oil. R_f 0.45 (hexane–dichloromethane, 1:1). IR spectrum, ν, cm^{-1}: 1170 (C–N), 1433 (CH_3), 1461 (CH_2), 2118 (C≡C), 2859 (CH_2), 2933 (CH_3). ^1H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 0.93 (3H, t, *J* = 7.5, CH_3); 1.38–1.44 (4H, m, $(C{\equiv}CCH_2CH_2C\underline{H}_2)_2$); 1.49–1.56 (6H, m, $(C{\equiv}CCH_2C\underline{H}_2CH_2)_2$, $C\underline{H}_2CH_2N$); 2.19–2.22 (4H, m, $N(CH_2C{\equiv}CC\underline{H}_2)_2$); 2.47 (2H, t, *J* = 7.5, $CH_2C\underline{H}_2N$); 3.39 (4H, s, $N(C\underline{H}_2C{\equiv}C)_2$). ^{13}C NMR spectrum (125 MHz), δ, ppm: 11.96 (CH_3); 18.7 ($2C{\equiv}C\underline{C}H_2$); 20.7 ($\underline{C}H_2CH_3$); 28.4 ($2C{\equiv}CCH_2CH_2\underline{C}H_2$); 28.8 ($2C{\equiv}CCH_2\underline{C}H_2$); 42.5 ($N(\underline{C}H_2C{\equiv}C)_2$); 54.9 ($CH_2\underline{C}H_2N$); 75.1 ($N(CH_2\underline{C}{\equiv}C)_2$); 84.9 ($N(CH_2C{\equiv}\underline{C})_2$). Mass spectrum, *m*/*z* (I_{rel}, %): 217 $[M]^+$ (10), 202 $[M–CH_3]^+$ (3), 188 $[M–CH_2CH_3]^+$ (100), 174 $[M–CH_3(CH_2)_2]^+$ (3), 160 $[M–N(CH_2)_3CH_3]^+$ (3), 91 $[NH(CH_2C{\equiv}C)_2]^+$ (18). Found, %: C 82.94; H 10.61; N 6.45. $C_{15}H_{23}N$. Calculated, %: C 82.89; H 10.67; N 6.44.

1-Butyl-3,4,8,9-tetradehydro-1,2,5,6,7,10-hexahydroazecine (3c). Yield 0.085 g (45%), yellow oil. R_f 0.53 (cyclohexane–ethyl acetate–CH_2Cl_2, 1:10:2). IR spectrum, ν, cm^{-1}: 1110 (C–N), 1432 (CH_3), 1455 (CH_2), 2220 (C≡C), 2861 (CH_2), 2931 (CH_3). ^1H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 0.94 (3H, t, *J* = 9.0, CH_3); 1.33–1.39 (2H, m, $C\underline{H}_2CH_3$); 1.40–1.49 (2H, m, $C\underline{H}_2CH_2CH_3$); 1.71–1.76 (2H, m, $(C{\equiv}CCH_2)_2C\underline{H}_2$); 2.32–2.35 (4H, m, $(C{\equiv}CC\underline{H}_2)_2CH_2$); 2.50 (2H, t, *J* = 9.0, $CH_2C\underline{H}_2N$); 3.38 (4H, s, $N(C\underline{H}_2C{\equiv}C)_2$). ^{13}C NMR spectrum (125 MHz), δ, ppm: 14.0 (CH_3); 18.0 ($(C{\equiv}C\underline{C}H_2)_2CH_2$); 20.6 ($\underline{C}H_2CH_3$); 28.2 ($(C{\equiv}CCH_2)_2\underline{C}H_2$); 29.6 ($\underline{C}H_2CH_2CH_3$); 42.6 ($N(\underline{C}H_2C{\equiv}C)_2$); 52.7 ($CH_2\underline{C}H_2N$); 75.6 ($N(CH_2\underline{C}{\equiv}C)_2$); 84.0 ($N(CH_2C{\equiv}\underline{C})_2$). Mass spectrum, *m*/*z* (I_{rel}, %): 188 $[M–H]^+$ (6), 174 $[M–CH_3]^+$ (6), 146 $[M–(CH_2)_2CH_3]^+$ (100), 117 $[M–NH(CH_2)_3CH_3]^+$ (45), 103

$[M–CH_3(CH_2)_3NHCH_2]^+$ (13), 91 $[NH(CH_2C{\equiv}C)_2]^+$ (83). Found, %: C 82.53; H 10.07; N 7.35. $C_{13}H_{19}N$. Calculated, %: C 82.48; H 10.12; N 7.40.

1-Butyl-1-azacycloundeca-3,9-diyne (3d). Yield 0.132 g (65%), yellow oil. R_f 0.60 (hexane–ethyl acetate, 1:2). IR spectrum, ν, cm^{-1}: 1111 (C–N), 1325 (C–N), 1385 (CH_3), 1432 (CH_3), 1458 (CH_2), 2230 (C≡C), 2863 (CH_2), 2931 (CH_3). ^1H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 0.94 (3H, t, *J* = 7.2, CH_3); 1.33–1.38 (2H, m, $C\underline{H}_2CH_3$); 1.40–1.48 (2H, m, $C\underline{H}_2CH_2CH_3$); 1.63–1.65 (4H, m, $(C{\equiv}CCH_2C\underline{H}_2)_2$); 2.24 (4H, br. s, $(C{\equiv}CC\underline{H}_2CH_2)_2$); 2.50 (2H, t, *J* = 7.2, $CH_2C\underline{H}_2N$); 3.38 (4H, s, $N(C\underline{H}_2C{\equiv}C)_2$). ^{13}C NMR spectrum (100 MHz), δ, ppm: 14.0 (CH_3); 18.2 ($2C{\equiv}C\underline{C}H_2CH_2$); 20.6 ($\underline{C}H_2CH_3$); 27.9 ($2C{\equiv}CCH_2\underline{C}H_2$); 29.6 ($\underline{C}H_2CH_2CH_3$); 42.5 ($N(\underline{C}H_2C{\equiv}C)_2$); 52.6 ($CH_2\underline{C}H_2N$); 75.3 ($N(CH_2\underline{C}{\equiv}C)_2$); 84.4 ($N(CH_2C{\equiv}\underline{C})_2$). Mass spectrum, *m*/*z* (I_{rel}, %): 202 $[M–H]^+$ (9), 160 $[M–(CH_2)_2CH_3]^+$ (100), 117 $[M–CH_2NH(CH_2)_3CH_3]^+$ (38), 91 $[M–N(CH_2C{\equiv}C)_2]^+$ (51). Found, %: C 82.74; H 10.45; N 6.92. $C_{14}H_{21}N$. Calculated, %: C 82.70; H 10.41; C 6.89.

1-Butyl-1-azacyclotrideca-3,11-diyne (3e). Yield 0.167 g (72%), yellow oil. R_f 0.45 (cyclohexane–ethyl acetate–CH_2Cl_2, 1:10:2). IR spectrum, ν, cm^{-1}: 1111, 1144 (C–N), 1361 (CH_3), 1436 (CH_2), 2261 (C≡C), 2857 (CH_2), 2930 (CH_3). ^1H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 0.94 (3H, t, *J* = 7.2 CH_3); 1.35–1.38 (2H, m, $C\underline{H}_2CH_3$); 1.39–1.43 (4H, m, $(C{\equiv}CCH_2CH_2C\underline{H}_2)_2$); 1.44–1.49 (2H, m, $C\underline{H}_2CH_2CH_3$); 1.51–1.53 (4H, m, $(C{\equiv}CCH_2C\underline{H}_2CH_2)_2$); 2.21 (4H, t, *J* = 7.0 $(C{\equiv}CC\underline{H}_2CH_2CH_2)_2$); 2.50 (2H, t, *J* = 7.5, $CH_2C\underline{H}_2N$); 3.38 (4H, s, $N(C\underline{H}_2C{\equiv}C)_2$). ^{13}C NMR spectrum (125 MHz), δ, ppm: 14.0 (CH_3); 18.7 ($2C{\equiv}C\underline{C}H_2CH_2CH_2$); 20.7 ($\underline{C}H_2CH_3$); 28.4 ($2C{\equiv}CCH_2CH_2\underline{C}H_2$); 28.8 ($2C{\equiv}CCH_2\underline{C}H_2CH_2$); 29.6 ($\underline{C}H_2CH_2CH_3$); 42.6 ($N(\underline{C}H_2C{\equiv}C)_2$); 52.6 ($CH_2\underline{C}H_2N$); 75.1 ($N(CH_2\underline{C}{\equiv}C)_2$); 84.9 ($N(CH_2C{\equiv}\underline{C})_2$). Mass spectrum, *m*/*z* (I_{rel}, %): 231 $[M]^+$ (6), 207 $[M–C{\equiv}C]^+$ (27), 188 $[M–(CH_2)_2CH_3]^+$ (87), 40 $[CNCH_2]^+$ (100). Found, %: C 83.11; H 10.92; N 6.01. $C_{16}H_{25}N$. Calculated, %: C 83.06; H 10.89; N 6.05.

1-*tert*-Butyl-3,4,8,9-tetradehydro-1,2,5,6,7,10-hexahydroazecine (3f). Yield 0.12 g (63%), yellow oil. R_f 0.38 (hexane–ethyl acetate–CH_2Cl_2, 1:2:1). IR spectrum, ν, cm^{-1}: 1018 (C–N), 1366 (CH_3), 1392 (CH_3), 1453 (CH_3), 2118 (C≡C), 2200 (C≡C), 2910 (CH_2), 2960 (CH_3). ^1H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 1.20 (9H, s, $3CH_3$); 1.68–1.76 (2H, m, $(C{\equiv}CCH_2)_2C\underline{H}_2$); 2.29–2.36 (4H, m, $(C{\equiv}CC\underline{H}_2)_2$); 3.60 (4H, s, $N(C\underline{H}_2C{\equiv}C)_2$). ^{13}C NMR spectrum (125 MHz), δ, ppm: 18.2 ($(2C{\equiv}C\underline{C}H_2)_2$); 27.5 ($(CH_3)_3$); 28.0 ($(C{\equiv}CCH_2)_2\underline{C}H_2$); 36.8 ($N(\underline{C}H_2C{\equiv}C)_2$); 55.0 ($\underline{C}(CH_3)_3$); 78.1 ($N(CH_2\underline{C}{\equiv}C)_2$); 83.3 ($N(CH_2C{\equiv}\underline{C})_2$). Mass spectrum, *m*/*z* (I_{rel}, %): 189 $[M]^+$ (9), 174 $[M–CH_3]^+$ (100), 144 $[M–3(CH_3)]^+$ (13), 132 $[M–C(CH_3)]^+$ (30), 117 $[M–NHC(CH_3)_3]^+$ (40), 91 $[NH(CH_2C{\equiv}C)_2]^+$ (45). Found, %: C 82.61; H 10.08; N 7.43. $C_{13}H_{19}N$. Calculated, %: C 82.48; H 10.12; N 7.40.

1-(*tert*-Butyl)-1-azacycloundeca-3,9-diyne (3g). Yield 0.103 g (51%), yellow oil. R_f 0.48 (hexane–ethyl acetate–CH_2Cl_2, 1:2:1). IR spectrum, ν, cm^{-1}: 1202 ($C(CH_3)_3$), 1262 (C–N), 1364 (CH_3), 1390 (CH_3), 1431 (CH_3), 1457 (CH_2), 2130 (C≡C), 2863 (CH_2), 2938 (CH_3). ^1H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 1.17 (9H, s, $3CH_3$); 1.59–1.62 (4H, m, $(CH_2C\underline{H}_2)_2$); 2.20 (4H, br. s, $(C\underline{H}_2CH_2)_2$); 3.57 (4H, s, $N(C\underline{H}_2C{\equiv}C)_2$). ^{13}C NMR spectrum (100 MHz), δ, ppm: 18.5 ($2C{\equiv}C\underline{C}H_2CH_2$); 27.5 ($CH_3$); 27.9 ($(C{\equiv}CCH_2\underline{C}H_2)_2$); 36.7 ($N(\underline{C}H_2)_2$); 54.9 ($N\underline{C}(CH_3)_3$); 77.8 ($N(CH_2\underline{C}{\equiv}C)_2$); 83.7 ($N(CH_2C{\equiv}\underline{C})_2$). Mass spectrum, *m*/*z* (I_{rel}, %): 203 $[M]^+$ (7), 188 $[M–CH_3]^+$ (100), 146 $[M–C(CH_3)_3]^+$ (9), 117 $[M–CH_2NHC(CH_3)_3]^+$ (16), 91 $[NH(CH_2C{\equiv}C)_2]^+$ (29). Found, %: C 82.83; H 10.52; N 6.84. $C_{14}H_{21}N$. Calculated, %: C 82.70; H 10.41; N 6.89.

A Supplementary information file containing ^1H and ^{13}C NMR spectra of compounds **3b** and **3e** is available at the journal website at http://link.springer.com/journal/10593.

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