



Supporting Information

for

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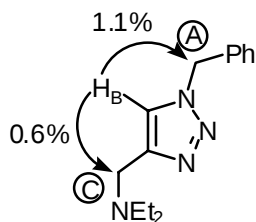
69451 Weinheim, Germany

“A Stepwise Huisgen Cycloaddition Process Catalyzed by Copper(I): Regioselective Ligation of Azides and Terminal Alkynes”

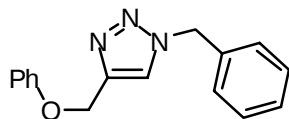
V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless

NOE experiments

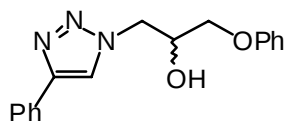
The geometry of 1*H*-1,2,3-triazoles was established by NOE experiments: irradiation of the triazole proton (H_B) gave enhancement of *both* H_A and H_C protons in 1,4-disubstituted isomers, which is not observed for 1,5-isomers.



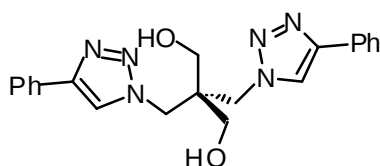
Compound Characterization data



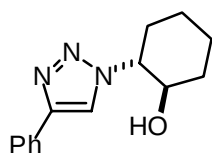
1-Benzyl-4-phenoxyethyl-1*H*-[1,2,3]triazole. White solid. ^1H NMR (399 MHz, CDCl_3 , δ): 5.15 (s, 2H, $-\text{CH}_2-$), 5.49 (s, 2H, $-\text{CH}_2-$), 6.93 (m, 3H, Ar *H*), 7.24 (m, 4H, Ar *H*), 7.34 (m, 3H, Ar *H*), 7.50 (s, 1H, triazole *H*). ^{13}C NMR (100 MHz, CDCl_3 , δ): 54.45, 62.22, 114.95, 121.46, 122.81, 128.33, 129.02, 129.36, 129.76, 134.67, 144.88, 158.38. LC-MS *m/z* (ion): 266.1 ($\text{M}+\text{H}^+$), 288.1 ($\text{M}+\text{Na}^+$).



(±)-1-Phenoxy-3-(4-phenyl-[1,2,3]triazol-1-yl)-propan-2-ol. White solid. ^1H NMR (399 MHz, $\text{DMSO-}d_6/\text{CDCl}_3$, δ): 3.88 (m, 2H, $-\text{CH}_2\text{OPh}$), 4.25 (m, 1H, CHOH), 4.44 (dd, 1H, $^3J_{\text{HH}} = 14$ and 7.2 Hz, triazole- CH_2-), 4.62 (dd, 1H, $^3J_{\text{HH}} = 14$ and 3.2 Hz, triazole- CH_2-), 5.46 (d, 1H, $^3J_{\text{HH}} = 3.6$ Hz, CHOH), 6.83 (m, 3H, OPh H), 7.15-7.22, (m, 3H, OPh H and triazole-Ph H), 7.30 (pseudo t, 2H, $J_{\text{app}} = 8$ Hz, triazole-Ph H), 7.71 (pseudo d, 2H, $J_{\text{app}} = 8$ Hz, triazole-Ph H), 8.05 (s, 1H, triazole H). ^{13}C NMR (99.75 MHz, CDCl_3 , δ): 53.5, 68.5, 69.5, 114.8, 121.3, 122.1, 125.7, 128.2, 129.1, 129.8, 131.1, 147.2, 158.7. LC-MS m/z (ion): 296.1 ($\text{M}+\text{H}^+$), 318.1 ($\text{M}+\text{Na}^+$).



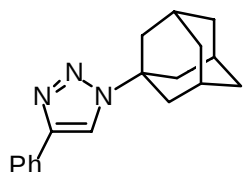
2,2-Bis-(4-phenyl-[1,2,3]triazol-1-ylmethyl)-propane-1,3-diol. White solid. ^1H NMR (399 MHz, $\text{DMSO-}d_6$, δ): 3.24 (d, $^3J_{\text{HH}} = 4.8$ Hz, 4H, $-\text{CH}_2\text{OH}$), 4.50 (s, 4H, $-\text{CH}_2\text{Triazole}$), 5.09 (t, $^3J_{\text{HH}} = 4.8$ Hz, 2H, $-\text{CH}_2\text{OH}$), 7.33 (pseudo t, $J_{\text{app}} = 7.6$ Hz, 2H, $p\text{-H}$ in Triazole- C_6H_5), 7.44 (pseudo t, $J_{\text{app}} = 7.6$ Hz, 4H, $m\text{-H}$ in Triazole- C_6H_5), 7.86 (pseudo d, $J_{\text{app}} = 7.6$ Hz, 4H, $o\text{-H}$ in Triazole- C_6H_5), 8.51 (s, 2H, triazole H). ^{13}C NMR (99.75 MHz, $\text{DMSO-}d_6$, δ): 45.45, 49.76, 59.96, 123.25, 125.23, 127.89, 128.91, 130.67, 146.04. LC-MS m/z (ion): 391.2 ($\text{M}+\text{H}^+$), 413.2 ($\text{M}+\text{Na}^+$).



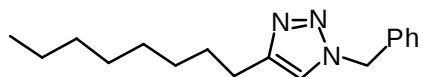
(±)-*trans*-2-(4-Phenyl-[1,2,3]triazol-1-yl)-cyclohexanol. Yellow solid. ^1H NMR (399 MHz, $\text{DMSO-}d_6/\text{CDCl}_3$, δ): 1.36 (m, 3H, cyclohexyl H), 1.75-2.16 (m, 5H, cyclohexyl H), 3.77 (m, 1H, cyclohexyl CH), 4.16 (pseudo ddd, $J_{\text{app}} = 4.0, 9.7, 12.3$ Hz, 1H, cyclohexyl CH), 4.76 (d, $^3J_{\text{HH}} = 5.7$ Hz, 1H, OH), 7.21 (pseudo t, $J_{\text{app}} = 7$ Hz, 1H, Ar H), 7.32 (pseudo t,

$J_{\text{app}} = 8 \text{ Hz}$, 2H, Ar H), 7.74 (pseudo d, $J_{\text{app}} = 7.4 \text{ Hz}$, 2H, Ar H), 7.98 (s, 1H, triazole H).

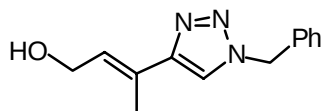
^{13}C NMR (100 MHz, $\text{DMSO-}d_6/\text{CDCl}_3$, δ): 24.63, 25.27, 32.45, 35.22, 67.11, 72.37, 120.31, 125.63, 128.0, 129.0, 131.32, 146.57. LC-MS m/z (ion): 244.1 ($\text{M}+\text{H}^+$), 266.1 ($\text{M}+\text{Na}^+$).



4-Phenyl-1-(adamant-1-yl)-1H-[1,2,3]triazole. White solid. ^1H NMR (399 MHz, CDCl_3 , δ): 1.78 (s, 6H, adamantyl H), 2.26 (s, 9H, adamantyl H), 7.28 (t, $^3J_{\text{HH}} = 7.2 \text{ Hz}$, Ar H), 7.38 (pseudo t, 2H, Ar H), 7.80 (m, 3H, triazole H and Ar H). ^{13}C NMR (99.75 MHz, CDCl_3 , δ): 29.7, 36.1, 43.2, 59.8, 116.2, 125.8, 128.0, 129.0, 131.3, 146.9. LC-MS m/z (ion): 280.2 ($\text{M}+\text{H}^+$), 302.2 ($\text{M}+\text{Na}^+$).

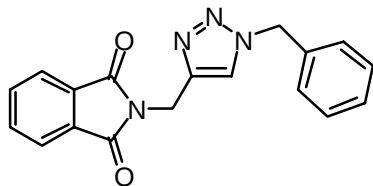


1-Benzyl-4-octyl-1H-[1,2,3]triazole. White solid. ^1H NMR (300 MHz, CD_3OD , δ): 0.89 (t, $^3J_{\text{HH}} = 6.6 \text{ Hz}$, 3H, $-\text{CH}_3$), 1.3 (m, 10H, $-\text{CH}_2-$), 1.65 (m, 2H, $-\text{CH}_2-$), 2.67 (t, $^3J_{\text{HH}} = 7.5 \text{ Hz}$, 2H, $-\text{CH}_2-$), 5.54 (s, 2H, $-\text{CH}_2\text{Ph}$), 7.23-7.36 (m, 5H, Ar H), 7.70 (s, 1H, triazole H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 14.28, 22.83, 25.93, 29.37, 29.44, 29.48, 29.59, 32.0, 54.12, 120.70, 128.11, 128.74, 129.20, 135.25, 149.18. LC-MS m/z (ion): 272.2 ($\text{M}+\text{H}^+$), 294.2 ($\text{M}+\text{Na}^+$).

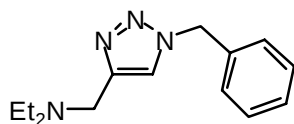


3-(1-Benzyl-1H-[1,2,3]triazol-4-yl)-but-2-en-1-ol. White solid. ^1H NMR (300 MHz, CDCl_3 , δ): 2.05 (s, 3H, $-\text{CH}_3$), 4.34 (d, $^3J_{\text{HH}} = 6 \text{ Hz}$, 2H, CH_2OH), 5.50 (s, 2H, $\text{PhCH}_2\text{Tiazole}$), 6.39 (t, $^3J_{\text{HH}} = 6 \text{ Hz}$, 1H, $-\text{CH}=\text{CH}-$), 7.26 (m, 2H, $-\text{C}_6\text{H}_5$), 7.35 (m, 3H, $-\text{C}_6\text{H}_5$), 7.38 (s, 1H, triazole H). ^{13}C NMR (75 MHz, CDCl_3 , δ): 15.4, 54.48, 59.45,

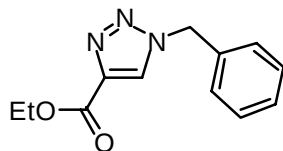
112.59, 119.58, 126.31, 128.12, 128.85, 129.23, 132.71, 144.04. LC-MS m/z (ion): 230.1 ($M+H^+$), 252.1 ($M+Na^+$).



2-(1-Benzyl-1H-[1,2,3]triazol-4-ylmethyl)-isoindole-1,3-dione. 1H NMR (399 MHz, DMSO- d_6 /CD $_3$ CN, δ): 5.22 (s, 2H, $-CH_2-$), 5.56 (s, 2H, $-CH_2-$), 7.22 (m, 2H, Ar H), 7.32 (m, 3H, Ar H), 7.78 (m, 4H, Ar H), 8.21 (s, 1H, triazole H). ^{13}C NMR (100 MHz, DMSO- d_6 , δ): 53.37, 69.96, 123.86, 127.07, 128.21, 128.67, 129.04, 129.34, 135.44, 136, 65, 141.33, 163.64. LC-MS m/z (ion): 319.1 ($M+H^+$), 341.1 ($M+Na^+$).



(1-Benzyl-1H-[1,2,3]triazol-4-ylmethyl)-diethylamine. Yellow oil. 1H NMR (300 MHz, CD $_3$ OD, δ): 1.09 (t, $^3J_{HH} = 6.9$ Hz, 6H, $-CH_3$ in $-NEt_2$), 2.51 (br q, $^3J_{HH} = 6.9$ Hz, 4H, $-CH_2-$ in $-NEt_2$), 3.78 (br s, 2H, $-CH_2-$), 5.58 (s, 2H, $-CH_2Ph$), 7.33 (m, 5H, Ar H), 7.87 (s, 1H, triazole H). ^{13}C NMR (100 MHz, CDCl $_3$, δ): 12.01, 46.92, 47.83, 54.19, 122.56, 128.15, 128.80, 129.22, 135.01, 145.89. LC-MS m/z (ion): 245.2 ($M+H^+$), 267.2 ($M+Na^+$).



1-Benzyl-1H-[1,2,3]triazole-4-carboxylic acid ethyl ester. White solid. 1H NMR (399 MHz, CDCl $_3$, δ): 1.34 (t, $^3J_{HH} = 7.2$ Hz, 3H, $-CH_2CH_3$), 4.35 (q, $^3J_{HH} = 7.2$ Hz, 3H, $-CH_2CH_3$), 5.53 (s, 2H, $-CH_2Ph$), 7.24 (m, 2H, Ar H), 7.34 (m, 3H, Ar H), 7.94 (s, 1H, triazole H). ^{13}C NMR (100 MHz, CDCl $_3$, δ): 14.5, 54.7, 61.5, 127.5, 128.5, 129.3, 129.5, 133.9, 140.9, 160.9. LC-MS m/z (ion): 232.1 ($M+H^+$), 254.1 ($M+Na^+$).