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Regioselective quaternization of *N*-alkyl-4-nitro-1,2,3-triazoles in $Bu^tOH–HClO_4$ system

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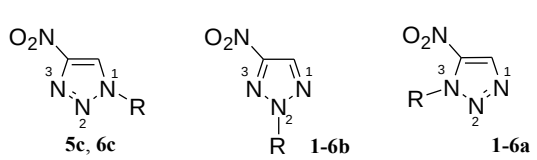

1a-b, **7** R = Me
2a-b, **8** R = Et
3a-b, **9** R = *n*-Pr
4a-b, **10** R = *cyclo*-C_6H_{11}
5a-c, **11** R = *i*-Pr
6a-c, **12** R = *s*-Bu

Structures and the numbering of the isomers of N-alkyl-4-nitro-1,2,3-triazoles

Preparation of components and reagents.

N-alkyl-4-nitro-1,2,3-triazoles were synthesized by the known procedures: *N*-ethyl-4-nitro-1,2,3-triazoles **2a-b** – ref. 4a, *N*-*i*-propyl-4-nitro-1,2,3-triazoles **5a-c** and *N*-*sec*-butyl-4-nitro-1,2,3-triazoles **6a-c** – ref. 6b.

*N*1-, *N*2- и *N*3-methyl-4-nitro-1,2,3-triazoles were synthesized by alkylation of 4-nitro-1,2,3-triazole sodium salt with dimethyl sulfate according to the procedure in ref. 4a. *N*2- and *N*3-isomers **1a-b** were isolated by hexane extraction followed by the solvent removal.

*N*1-, *N*2- and *N*3-*n*-propyl-4-nitro-1,2,3-triazoles were synthesized by alkylation of 4-nitro-1,2,3-triazole sodium salt with n-propyl bromide according to the procedure in ref. 4a. *N*2- and N3-isomers **3a-b** were isolated by vacuum distillation (132–136°C/18–20 mmHg).

*N*1-, *N*2- и *N*3-cyclohexyl-4-nitro-1,2,3-triazoles were synthesized by alkylation of 4-nitro-1,2,3-triazole with cyclohexanol in conc. H_2SO_4 according to the procedure in ref. 6b. *N*2- and *N*3-isomers **4a-b** were isolated by vacuum distillation (112–113°C/1–2 mmHg).

The ratios of **1a/1b**, **2a/2b**, **3a/3b**, **4a/4b, 5a/5b/5c**, and **6a/6b/6c** were determined by the ^{1}H NMR spectra of integral signal intensities of singlet protons at C-5 endocyclic carbon atoms.

All other reagents (*tert*-butanol, perchloric acid) and solvents were obtained from commercial sources and used without purification.

Characteristics of compounds 7-12.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III spectrometer (400.13 and 100.61 MHz, respectively) in DMSO-d_6, internal standard DMSO-d_6. IR spectra (KBr): FT-801 FTIR spectrometer. Mass spectra were taken on a Shimadzu LCMS-8030 Triple Quadrupole Mass Spectrometer. The elemental analysis was carried out on a FlashEA 1112 analyzer. The melting point was determined on a Stuart SMP30 apparatus.

1-tert-*Butyl-3-methyl-4-nitro-1,2,3-triazolium perchlorate* **7**: compound **7** is identical in mp, spectral characteristics (^{1}H, ^{13}C NMR spectra) and elemental analysis to nitrotriazolium salt reported in ref. 5.

1-tert-*Butyl-3-ethyl-4-nitro-1,2,3-triazolium perchlorate* **8**: colorless crystals. ^{1}H NMR (ppm) δ: 10.37 (s, 1H, $C_{endocyclic}$-H); 4.97 (q, 2H, J=7.3 Hz, -CH_2-CH_3); 1.75 (s, 9H, *t*-butyl-CH_3); 1.61 (t, 3H, J=7.3 Hz, -CH_2-CH_3). ^{13}C NMR (ppm) δ: 145.47 (C-NO_2); 128.95 (C-H); 69.17 (C(CH_3)$_3$); 51.76 (CH_2); 28.64 (C(CH_3)$_3$); 13.52 (CH_3). FTIR (ν, cm^{-1}): 3126, 3102, 2997, 2949, 2025, 1580, 1543, 1475, 1438, 1379, 1353, 1328, 1294, 1192, 1167, 1088, 1030, 878, 840, 803, 747, 706, 689, 625, 585. MS (DUIS-ESI&APCI), m/z: 156 [$(CH_3)_2$CH-$C_2HN_4O_2$]$^+$; 170 [C(CH_3)$_3$-$C_2HN_4O_2$]$^+$; 184 [$(CH_3)_3$C-CH_3-$C_2HN_4O_2$-H]$^+$; 200 [$(CH_3)_3$C-C_2H_5-$C_2HN_4O_2$+H]$^+$; 211 [$(CH_3)_3$C-$C_2HN_4O_2$+CH_3CN]$^+$; 497 [2(C(CH_3)$_3$-C_2H_5-$C_2HN_4O_2$)+ClO_4]$^+$; 99 [ClO_4]$^-$; 397 [C(CH_3)$_3$-C_2H_5-$C_2HN_4O_2$+2ClO_4]$^-$. Found (%): C, 32.14; H, 5.12; N, 18.75. Calc. for $C_8H_{15}ClN_4O_6$ (%): C, 32.17; H, 5.06; N, 18.76.

1-tert-*Butyl-3*-n-*propyl-4-nitro-1,2,3-triazolium perchlorate* **9**: colorless crystals. ^{1}H NMR (ppm) δ: 10.37 (s, 1H, $C_{endocyclic}$-*H*); 4.90 (t, 2H, J=7.0 Hz, *n*-propyl-CH_2-); 2.05 (sextet, 2H, *n*-propyl-CH_2-); 1.75 (s, 9H, *t*-butyl-CH_3); 1.00 (t, 3H, J=7.4 Hz, *n*-propyl-CH_3-). ^{13}C NMR (ppm) δ: 145.34 (C-NO_2); 129.08 (C-H); 69.17 (C(CH_3)$_3$); 57.15 (CHCH_2CH_3); 28.57(C(CH_3)$_3$); 21.47 (CHCH_2CH_3); 10.93 (CHCH_2CH_3). FTIR (ν, cm^{-1}): 3126, 3098, 3080, 2981, 2882, 2020, 1584, 1547, 1469, 1434, 1410, 1381, 1368, 1333, 1305, 1287, 1241, 1191, 1169, 1092, 1029, 909, 879, 842, 762, 746, 697, 625, 576. MS (DUIS-ESI&APCI), m/z: 156 [$(CH_3)_2$CH-$C_2HN_4O_2$]$^+$; 170 [C(CH_3)$_3$-$C_2HN_4O_2$]$^+$; 184

$[(CH_3)_3C\text{-}CH_3\text{-}C_2HN_4O_2\text{-}H]^+$; 198 $[(CH_3)_3C\text{-}C_2H_5\text{-}C_2HN_4O_2\text{-}H]^+$; 213 $[(CH_3)_3C\text{-}C_3H_7\text{-}C_2HN_4O_2]^+$; 225 $[(CH_3)_3C\text{-}CH_3\text{-}C_2HN_4O_2+CH_3CN\text{-}H]^+$; 525 $[2(C(CH_3)_3\text{-}C_3H_7\text{-}C_2HN_4O_2)+ClO_4]^+$; 99 $[ClO_4]^-$; 411 $[C(CH_3)_3\text{-}C_3H_7\text{-}C_2HN_4O_2+2ClO_4]^-$. Found (%): C, 34.47; H, 5.52; N, 17.85. Calc. for $C_9H_{17}ClN_4O_6$ (%): C, 34.57; H, 5.48; N, 17.92.

1-tert-*Butyl-3-cyclohexyl-4-nitro-1,2,3-triazolium perchlorate* **10**: colorless crystals. ^{1}H NMR (ppm) δ: 10.38 (s, 1H, $C_{endocyclic}$-*H*); 5.33 (m, 1H, cyclohexyl-*C*H); 2.29-1.33 (m, 10H, cyclohexyl-$(CH_2)_5$); 1.75 (s, 9H, C(*C*$H_3)_3$). ^{13}C NMR (ppm) δ: 145.27 (*C*-NO_2); 129.04 (*C*-H); 65.96 (*C*$(CH_3)_3$); 59.12 (cyclohexyl-*C*H); 32.14 (cyclohexyl-*C*H_2); 28.63 (C(*C*$H_3)_3$); 24.79 (cyclohexyl-*C*H_2); 23.13 (cyclohexyl-*C*H_2). FTIR (ν, cm^{-1}): 3126, 3102, 2944, 2863, 2024, 1581, 1543, 1451, 1380, 1351, 1334, 1268, 1240, 1189, 1158, 1132, 1093, 1034, 1001, 935, 897, 863, 842, 813, 745, 702, 625, 582. MS (DUIS-ESI&APCI), m/z: 156 $[(CH_3)_2CH\text{-}C_2HN_4O_2]^+$; 197 $[(CH_3)_2CH\text{-}C_2HN_4O_2+CH_3CN]^+$; 211 $[CH_3\text{-}cyclo\text{-}C_6H_{11}\text{-}C_2HN_4O_2]^+$; 225 $[C_2H_5\text{-}cyclo\text{-}C_6H_{11}\text{-}C_2HN_4O_2]^+$; 239 $[(CH_3)_2CH\text{-}cyclo\text{-}C_6H_{11}\text{-}C_2HN_4O_2]^+$; 253 $[(CH_3)_3C\text{-}cyclo\text{-}C_6H_{11}\text{-}C_2HN_4O_2]^+$; 279 $[(CH_3)_2CH\text{-}cyclo\text{-}C_6H_{11}\text{-}C_2HN_4O_2+CH_3CN\text{-}H]^+$; 605 $[2((CH_3)_3C\text{-}cyclo\text{-}C_6H_{11}\text{-}C_2HN_4O_2)+ClO_4]^+$; 631 $[(CH_3)_3C\text{-}cyclo\text{-}C_6H_{11}\text{-}C_2HN_4O_2+(CH_3)_2CH\text{-}cyclo\text{-}C_6H_{11}\text{-}C_2HN_4O_2+CH_3CN+ClO_4\text{-}H]^+$; 99 $[ClO_4]^-$; 451 $[(CH_3)_3C\text{-}cyclo\text{-}C_6H_{11}\text{-}C_2HN_4O_2+2ClO_4]^-$. Found (%): C, 40.59; H, 5.95; N, 15.72. Calc. for $C_{12}H_{21}ClN_4O_6$ (%): C, 40.86; H, 6.00; N, 15.88.

1-tert-*Butyl-3-isopropyl-4-nitro-1,2,3-triazolium perchlorate* **11**: colorless crystals. ^{1}H NMR (ppm) δ: 10.35 (s, 1H, $C_{endocyclic}$-*H*); 5.67 (m, 1H, *i*-propyl-C*H*$(CH_3)_2$); 1.75 (s, 9H, C(C*H*$_3)_3$); 1.67 (d, 6H, *J*=6.5 Hz, *i*-propyl-CH(C*H*$_3)_2$). ^{13}C NMR (ppm) δ: 145.20 (*C*-NO_2), 129.04 (*C*-H), 69.22 (*C*$(CH_3)_3$), 60.78 (*C*H$(CH_3)_2$), 28.58(C(*C*$H_3)_3$), 21.79 (CH(*C*$H_3)_2$). FTIR (ν, cm^{-1}): 3122, 3096, 2996, 2948, 2880, 2018, 1579, 1538, 1443, 1472, 1398, 1381, 1342, 1299, 1262, 1228, 1183, 1136, 1090, 1031, 886, 840, 747, 706, 625, 562. MS (DUIS-ESI&APCI), m/z: 156 $[(CH_3)_2CH\text{-}C_2HN_4O_2]^+$; 170 $[C(CH_3)_3\text{-}C_2HN_4O_2]^+$; 184 $[(CH_3)_3C\text{-}CH_3\text{-}C_2HN_4O_2\text{-}H]^+$; 198 $[(CH_3)_3C\text{-}C_2H_5\text{-}C_2HN_4O_2\text{-}H]^+$; 213 $[(CH_3)_3C\text{-}(CH_3)_2CH\text{-}C_2HN_4O_2]^+$; 225 $[(CH_3)_3C\text{-}CH_3\text{-}C_2HN_4O_2+CH_3CN\text{-}H]^+$; 525 $[2(C(CH_3)_3\text{-}(CH_3)_2CH\text{-}C_2HN_4O_2)+ClO_4]^+$; 99 $[ClO_4]^-$; 411 $[C(CH_3)_3\text{-}(CH_3)_2CH\text{-}C_2HN_4O_2+2ClO_4]^-$. Found (%): C, 34.88; H, 5.38; N, 17.59. Calc. for $C_9H_{17}ClN_4O_6$ (%): C, 34.57; H, 5.48; N, 17.92.

1-tert-*Butyl-3*-sec-*butyl-4-nitro-1,2,3-triazolium perchlorate* **12**: colorless crystals. ^{1}H NMR (ppm) δ: 10.38 (s, 1H, $C_{endocyclic}$-*H*); 5.53 (m, 1H, *s*-butyl-C*H*-); 2.12-

1.95 (m, 2H, *s*-butyl-CH_2-); 1.75 (s, 9H, C(CH_3)$_3$); 1.64 (d, 3H, *J* =6.5 Hz, *s*-butyl-CH_3); 0.94 (t, 3H, *J*=7.3 Hz, *s*-butyl-CH_3). ^{13}C NMR (ppm) δ: 145.51 (*C*-NO_2); 129.24 (C_5-H); 69.25 (*C*H(CH_3)CH_2CH_3); 65.23 *C*(CH_3)$_3$); 28.65 CH(CH_3)*C*H_2CH_3; 28.62(C(*C*H_3)$_3$); 19.33 (CH(*C*H_3)CH_2CH_3); 9.94 (CH(CH_3)CH_2*C*H_3). FTIR (ν, cm^{-1}) 3135, 3109, 2990, 2946, 2887, 2022, 1582, 1543, 1466, 1409, 1380, 1338, 1304, 1241, 1227, 1187, 1133, 1094, 1033, 963, 871, 843, 802, 746, 706, 624, 566. MS (DUIS-ESI&APCI), m/z: 156 $[(CH_3)_2CH\text{-}C_2HN_4O_2]^+$; 197 $[(CH_3)_2CH\text{-}C_2HN_4O_2+CH_3CN]^+$; 212 $[(CH_3)_2CH\text{-}CH(CH_3)CH_2CH_3\text{-}C_2HN_4O_2\text{-}H]^+$; 228 $[(CH_3)_3C\text{-}CH(CH_3)CH_2CH_3\text{-}C_2HN_4O_2+H]^+$; 454 $[2((CH_3)_3C\text{-}CH(CH_3)CH_2CH_3\text{-}C_2HN_4O_2)]^+$; 555 $[2((CH_3)_3C\text{-}CH(CH_3)CH_2CH_3\text{-}C_2HN_4O_2)+ClO_4+2H]^+$; 99 $[ClO_4]^-$; 425 $[(CH_3)_3C\text{-}CH(CH_3)CH_2CH_3\text{-}C_2HN_4O_2+2ClO_4]^-$. Found (%): C, 37.10; H, 5.95; N, 17.31. Calc. for $C_{10}H_{19}ClN_4O_6$ (%): C, 36.76; H, 5.86; N, 17.15.