Supporting Information

Kinetics of Nucleophilic Substitution of Compounds Containing Multiple Leaving Groups Bound to a Neopentyl Skeleton

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Synthesis of compounds 2, 4, and 7

2-Methyl-2-(((methylsulfonyl)oxy)methyl)propane-1,3-diy1 dimethanesulfonate (2). 1,1,1-
Tris(hydroxymethyl)ethane 1 (1.0 g, 8.3 mmol) was suspended in CH₂Cl₂ (30 mL),
triethylamine (5.8 mL, 42 mmol) was added, and the mixture was cooled to 0 °C.
For 5 minutes, MsCl (2.6 mL, 33 mmol) was added dropwise, and the mixture was
stirred at 0 °C. After 1.5 hours, reaction completion was confirmed by NMR. The
mixture was extracted between CH₂Cl₂ and 1M HCl (both 50 mL). The organic
phase was dried with MgSO₄ (0.5 g). The crude product (1.97 g) was purified by column chromatography
(25 g silica gel) eluting with hexane/EtOAc 1/3. Fractions with the product were collected and evaporated
on a rotary evaporator at room temperature and then dried at room temperature using an oil rotary pump.
The product was obtained as a colorless oil, in 34% yield (1.0 g). IR(KBr): 3022, 2944, 1470, 1413, 1356,
1341, 1329, 1171, 1006 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 4.15 (s, 6H, H-3), 3.07 (s, 9H, H-4), 1.16 (s,
3H, H-1). ¹³C¹H NMR (CDCl₃, 101 MHz): δ 69.47 (C-1), 37.50 (C-4), 39.53 (C-3), 39.70 (C-2), 37.50 (C-4), 16.21 (C-1). MS (ESI) m/z: [M + Na]⁺ Calcd for C₆H₁₈O₆S₂Na 377.0; Found 377.0. HRMS (ESI/Q-TOF) m/z: [M + NH₄]⁺
Calcd for C₈H₂₂NO₆S₃ 372.0451; Found 372.0466. ¹H spectrum is in accordance with the literature¹.

2-Methyl-2-((tosyloxy)methyl)propane-1,3-diy1 bis(4-methylbenzenesulfonate) (4). 1,1,1-
Tris(hydroxymethyl)ethane 1 (10 g, 83.2 mmol) was dissolved in pyridine (40 mL). For 1 hour, TsCl (58
g, 300 mmol) in pyridine (180 mL) was added dropwise, and the mixture was stirred at room temperature for 12 hours. The reaction mixture was monitored by TLC using hexane/EtOAc 1/1 mixture.
The substances were detected by immersing the TLC plate in a basic potassium permanganate solution, followed by heating to 250 °C by a heat gun. The reaction mixture was poured into a mixture of water (80 mL), MeOH (160 mL), and concentrated HCl (64 mL).
The resulting precipitate was collected by filtration and washed with water and MeOH. The crude product
was dried at 55 °C using an oil rotary pump and then recrystallized from acetone (45 mL). The product was
collected by filtration and dried at room temperature using an oil rotary pump. The product was obtained
as a white crystalline powder, in 70% yield (33.8 g). IR(KBr): 3064, 3052, 3004, 2962, 2926, 1445,
1470, 1413, 1356, 1293, 1180, 1099 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.69 (m, 6H, H-5), 7.35 (m, 6H, H-6),
3.75 (s, 6H, H-3), 2.46 (s, 9H, H-8), 0.88 (s, 3H, H-1). ¹³C¹H NMR (CDCl₃, 101 MHz): δ 145.50 (C-4),
131.99 (C-7), 130.20 (C-6), 128.02 (C-5), 69.86 (C-3), 39.53 (C-2), 21.81 (C-8), 16.21 (C-1). UV-VIS
(MeOH), λₘₐₓ, nm: 201.5, λₘₐₓ₂, nm: 225.5, λₘₐₓ₃, nm: 262.0, λₘₐₓ₄, nm: 273.0, 1*10⁻⁵ M. MS (ESI) m/z:
[M + Na]⁺ Calcd for C₂₆H₃₀O₈S₄Na 605.1; Found 605.1. HRMS (ESI/Q-TOF) m/z: [M + Na]⁺ Calcd for
C₂₆H₃₀O₈S₄Na 605.0944; Found 605.0970. ¹H and ¹³C NMR spectra are in accordance with the literature².
1,3-Dichloro-2-(chloromethyl)-2-methylpropane (7). 1,1,1-Tris(hydroxymethyl)ethane 1 (5 g, 42 mmol) was dissolved in pyridine (10 mL). This solution and SOCl\(_2\) (9.7 mL, 133 mmol) were simultaneously added dropwise to pyridine (17 mL) cooled to 0 °C. After addition, the mixture was warmed to room temperature and then to 50 °C in an oil bath. After 1 hour, the mixture was warmed to 115 °C and kept under stirring for 4 hours. The reaction mixture was monitored by TLC using hexane/EtOAc 1/3 mixture for the starting compound. The substances were detected by immersing the TLC plate in a basic potassium permanganate solution, followed by heating to 250 °C by a heat gun. The reaction mixture was extracted between Et\(_2\)O and 1M HCl (both 70 mL). The organic phase was diluted with another 50 mL of Et\(_2\)O and subsequently extracted with brine (70 mL). The organic phase was dried with MgSO\(_4\) (0.5 g), filtered, and evaporated at room temperature on a rotary evaporator. The product was dried at room temperature using an oil rotary pump. The product was obtained as a colorless oil, in 81% yield (5.85 g). IR(KBr): 2968, 2923, 2845, 1559, 1410, 1365, 1174 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 400 MHz): δ 3.58 (s, 6H, H-3), 1.20 (s, 3H, H-1). \(^{13}\)C{\(^1\)H} NMR (CDCl\(_3\), 101 MHz): δ 48.46 (C-3), 42.13 (C-2), 19.48 (C-1). \(^1\)H and \(^{13}\)C NMR spectra are in accordance with the literature\(^3\).

**Preparation of tetramethylammonium and cesium azides**

**Preparation of cesium azide**

Sodium azide (2.60 g, 0.040 mol) was dissolved in water (50 mL) and poured into a strong cation exchanger column DOWEX 50W (60 mL, H\(^+\) form). The column was washed with water until the solution was weakly acidic. Cesium carbonate (5.2 g, 0.016 mol) was dissolved in water (100 mL), and the aqueous solution of hydrazoic acid was slowly poured into this solution. The solution was evaporated on a rotary evaporator at 50 °C. The product was dried at 70 °C using an oil rotary pump. The product was obtained as a white solid in 97% yield (5.48 g).

**Preparation of tetramethylammonium azide**

Sodium azide (3.12 g, 0.048 mol) was dissolved in water (50 mL) and poured into a strong cation exchanger column DOWEX 50W (60 mL, H\(^+\) form). The column was washed with water until the solution was weakly acidic. Tetramethylammonium bromide (5.0 g, 0.032 mol) was dissolved in water (50 mL) and poured into a strong anion exchanger column DOWEX 1-8 (60 mL, OH\(^-\) form). The column was washed with water until the solution was basic. Then, the aqueous solution of hydrazoic acid was slowly poured into this solution. The solution was evaporated on a rotary evaporator at 50 °C. The product was dried at 70 °C using an oil rotary pump. The product was obtained as a white solid in 98% yield (3.67 g).
Characterisation of compounds 2-7
2-Methyl-2-(((methylsulfonyl)oxy)methyl)propane-1,3-diyl dimethanesulfonate (MsO)_3Np (2)
Figure S1: ^1H NMR of (MsO)_3Np (2) (CDCl_3, 400 MHz)

Figure S2: ^13C(^1H) NMR of (MsO)_3Np (2) (CDCl_3, 101 MHz)
2-Methyl-2-(((trifluoromethyl)sulfonyl)oxy)methyl)propane-1,3-diyl bis(trifluoromethanesulfonate) (TfO)₃Np (3)

Figure S3: $^1$H NMR of (TfO)₃Np (3) (CDCl₃, 400 MHz) – crude

Figure S4: $^1$H NMR of (TfO)₃Np (3) (CDCl₃, 400 MHz) – column chromatography
Figure S5: $^{13}$C($^1$H) NMR of (TfO)$_3$Np (3) (CDCl$_3$, 101 MHz) – column chromatography

Figure S6: $^{19}$F NMR of (TfO)$_3$Np (3) (CDCl$_3$, C$_6$F$_6$, 376 MHz) – column chromatography
Figure S7: $^1$H NMR of (TsO)$_3$Np (4) (CDCl$_3$, 400 MHz)

Figure S8: $^{13}$C\{$^1$H} NMR of (TsO)$_3$Np (4) (CDCl$_3$, 101 MHz)
1,3-Diiodo-2-(iodomethyl)-2-methylpropane $\text{I}_3\text{Np}$ (5)

Figure S9: $^1$H NMR of $\text{I}_3\text{Np}$ (5) (CDCl$_3$, 400 MHz)

Figure S10: $^{13}$C{$^1$H} NMR of $\text{I}_3\text{Np}$ (5) (CDCl$_3$, 101 MHz)
1,3-Dibromo-2-(bromomethyl)-2-methylpropane Br₃Np (6)
Figure S11: $^1$H NMR of Br₃Np (6) (CDCl₃, 400 MHz)

Figure S12: $^{13}$C($^1$H) NMR of Br₃Np (6) (CDCl₃, 101 MHz)
1,3-Dichloro-2-(chloromethyl)-2-methylpropane Cl₃Np (7)

Figure S13: $^1$H NMR of Cl₃Np (7) (CDCl₃, 400 MHz)

Figure S14: $^{13}$C{$^1$H} NMR of Cl₃Np (7) (CDCl₃, 101 MHz)
Figure S15: Composition of the reaction mixture in reaction of (MsO)$_3$Np (2) with an excess of NaN$_3$ in time

Figure S16: Composition of the reaction mixture in reaction of (TfO)$_3$Np (3) with an excess of NaN$_3$ in time
Figure S17: Composition of the reaction mixture in reaction of I$_3$Np (5) with an excess of NaN$_3$ in time

![Graph showing the relative intensity of different compounds over time](image)

Figure S18: Composition of the reaction mixture in reaction of Br$_3$Np (6) with an excess of NaN$_3$ in time

![Graph showing the relative intensity of different compounds over time](image)
Figure S19: Composition of the reaction mixture in reaction of Cl$_3$Np (7) with an excess of NaN$_3$ in time

![Figure S19: Composition of the reaction mixture in reaction of Cl$_3$Np (7) with an excess of NaN$_3$ in time](image)

Figure S20: Composition of the reaction mixture in reaction of (TsO)$_3$Np (4) with an excess of CsN$_3$ in time

![Figure S20: Composition of the reaction mixture in reaction of (TsO)$_3$Np (4) with an excess of CsN$_3$ in time](image)
Figure S21: Composition of the reaction mixture in reaction of (TsO)$_3$Np (4) with an excess of (Me$_4$N)N$_3$ in time

![Graph showing the composition of the reaction mixture in reaction of (TsO)$_3$Np (4) with an excess of (Me$_4$N)N$_3$ in time.]

Figure S22: Composition of the reaction mixture in reaction of I$_3$Np (5) with an excess of CsN$_3$ in time

![Graph showing the composition of the reaction mixture in reaction of I$_3$Np (5) with an excess of CsN$_3$ in time.]

Figure S23: Composition of the reaction mixture in reaction of I$_3$Np (5) with an excess of (Me$_4$N)$_3$N in time.

Figure S24: Variation of concentration of (MsO)$_3$Np (2) and NaN$_3$ as a function of time.
Figure S25: Variation of concentration of I$_3$Np (5) and NaN$_3$ as a function of time

Figure S26: Variation of concentration of Br$_3$Np (6) and NaN$_3$ as a function of time
Figure S27: Variation of concentration of Cl$_3$Np (7) and NaN$_3$ as a function of time

Figure S28: Variation of concentration of (TsO)$_3$Np (4) and CsN$_3$ as a function of time
Figure S29: Variation of concentration of (TsO)$_3$Np (4) and (Me$_4$N)N$_3$ as a function of time

Figure S30: Variation of concentration of I$_3$Np (5) and CsN$_3$ as a function of time
Figure S31: Variation of concentration of $\text{I}_3\text{Np}$ (5) and $(\text{Me}_4\text{N})\text{N}_3$ as a function of time
Figure S32: A log-log graph depicting relationship between half-lives and rate constants of each X₃Np

Figure S33: Graphs of half-lives: A – compound I₃Np (5) with NaN₃, CsN₃, and (Me₄N)N₃; B – compound (TsO)₃Np (4) with NaN₃, CsN₃, and (Me₄N)N₃
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