CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Substituents Effects on the Electrophilic Activity of Nitroarenes in the Reactions with Carbanions

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Supplementary information

General

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 (400 MHz) or Brucker AM-500 (500 MHz) instruments. Chemical shifts are expressed in ppm referred to TMS, coupling constans in Hertz. Mass spectra were recorded on an AMD 604 Inectra GmbH (EI ionization) and Mariner (ESI ionization) spectrometers. GLC analyses were performed on HP 6890 chromatograph with HP-5 capillary column. Melting points are uncorrected.

Silica gel Merck 60 (230-400 mesh) was used for column chromatography. Kieselgel 60/F_{254} (Merck) plates on aluminum foil were used for TLC. All solvents used for column chromatography, extraction and crystallization were distilled. DMF was purified by distillation over CaH_2, THF was distilled over benzophenone potassium, extra pure DMSO was used. All reactions were carried out in argon atmosphere.

Most of the reagents were commercially available.

Isopropyl 4-nitro- and 2-nitrobenzoates were obtained according to known procedure from appriopriate acids.[1] Chloromethyl phenyl sulfone was synthetised according to known procedure.[2]

Preparative VNS reaction of nitroarenes with sulfone 1, general procedure

To a solution of *t*BuOK (1.02 g, 9 mmol) in THF or DMF (5 mL) cooled to -78°C (THF) or -40°C (DMF) a solution of chloromethyl phenyl sulfone (0.570 g, 3 mmol) and nitroarene (3 mmol) in THF or DMF was added. After 20 min the reaction mixture was quenched with acetic acid (3mL) or aqueous (1:10) HCl (5 mL), diluted with water (100 mL) and extracted with CH_2Cl_2. Combined extracts were washed with water, dried with Na_2SO_4. Products were isolated and purified by column chromatography or/and recrystallization.

The VNS reaction under thermodynamic conditions

To a solution of nitroarene (1 mmol) in DMSO (5 mL) at room tempetarure carbanion of chloromethyl phenyl sulfone generated from the solution of sulfone **1** (1.9 g, 10 mmol) in DMSO (20 mL) passed through a layer of grinded KOH was introduced during 10 minutes. The mixture was acidified with aqueous HCl (1:10) and products were isolated in the same way as in proceeding procedure.

Spectral data of products formed in VNS reaction between nitroarenes and sulfone 1

The most products of VNS reaction with chloromethyl phenyl sulfone are described in the literature.[2,3]

Reaction of 4-thiophenylnitrobenzene with 1 (1 product)

(2-nitro-5-phenylthio)benzyl phenyl sulfone: yield 79%; m.p. 147-149°C (EtOH); ^{1}H NMR (500 MHz, CDCl$_3$): *d* = 4.86 (s, 2H), 7.08 (d, *J* = 2.10, 1H), 7.12 (dd, *J* = 8.68, *J* = 2.10, 1H), 7.44-7.53 (m, 7H), 7.63-7.70 (m, 3H), 7.85 (d, *J* = 8.68, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): *d* = 58.66, 123.95, 126,14, 127.12, 128.38, 129.21, 129.81, 129.82, 130.08, 131.29, 134.11, 134.66, 137.98, 135.80, 147.24; MS (EI) *m/z* (%): 385 (75) [M^+], 244 (100), 214 (41), 184 (28), 171 (21), 109 (22), 77 (70), 51 (37); HRMS (EI): *m/z* calcd for $C_{19}H_{15}NO_4S_2$: 385.04425 [M^+]; found: 385.04334.

Reaction of 4-isopropylnitrobenzene with 1 (1 product)

(5-isopropyl-2-nitro)benzyl phenyl sulfone: yield 33%; yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$): *d* = 1.23 (d, *J* = 6.90, 6H), 2.96 (septet, *J* = 6.90, 1H), 4.96 (s, 2H), 7.18 (d, *J* = 1.92, 1H), 7.35 (dd, *J* = 8.52, *J* = 1.92, 1H), 7.45-7.50 (m, 2H), 7.60-7.70 (m, 3H), 7.94 (d, *J* = 8.52, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): *d* = 23.39, 33.88, 58.78, 123.08, 125.82, 127.89, 128.43, 129.18, 132.46, 134.03, 137.94, 147.14, 155.15; MS (EI) *m/z* (%): 273 (8), 178 (100), 105 (22), 77 (24); HRMS (ESI): *m/z* calcd for $C_{16}H_{17}NO_4NaS$: 342.07705 [M^+]; found: 342.07754.

Reaction of 4-carboisopropoxynitrobenzene with 1 (1 product)

(5-carboisopropoxy-2-nitro)benzyl phenyl sulfone: yield 68%; m.p.135-136°C (EtOH); ^{1}H NMR (400 MHz, CDCl$_3$): *d* = 1.39 (d, *J* = 6.25, 6H), 4.96 (s, 2H), 5.27 (septet, *J* = 6.25, 1H), 7.49-7.55 (m, 2H), 7.40-7.70 (m, 1H), 7.05-7.45 (m, 2H), 8.00 (d, *J* = 1.85, 1H), 8.02 (d, *J* = 8.46, 1H), 8.17 (dd, *J* = 8.46, *J* = 1.85, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): *d* = 21.83, 58.45, 69.99, 123.21, 125.52, 128.42, 129.37, 131.03, 134.29, 135.04, 135.27, 137.87, 151.70, 163.44; MS (EI) *m/z* (%): 304 (19), 222 (100), 180 (68), 77 (17); HRMS (ESI): *m/z* calcd for $C_{17}H_{17}NO_6NaS$: 386.0674 [M^+]; found: 386.0669.

Reaction of 1-nitronaphtalene with 1 (2 products)

(1-nitro-2-naphthyl)methyl phenyl sulfone: yield 87%; m.p. 210-212°C (EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 4.62 (s, 2H), 7.43-7.48 (m, 2H), 7.61-7.70 (m, 7H), 7.91-7.95 (m, 1H), 8.00 (d, *J* = 8.53, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 58.21, 118.54, 122.15, 124.42, 127.68, 128.10, 128.23, 128.47, 129.07, 129.28, 131.18, 133.75, 134.29, 137.64, 148.69; MS (EI) *m/z* (%): 327 (1) [M^+], 251 (20), 173 (41), 139 (19), 156 (100), 77 (21); HRMS (EI): *m/z* calcd for $C_{17}H_{13}NO_4S$: 327.05653 [M^+]; found: 327.05588.

(4-nitro-1-naphthyl)methyl phenyl sulfone: yield 6%; m.p. 270-271°C (EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 5.13 (s, 2H), 7.35-8.30 (m, 10H), 8.43 (d, *J* = 8.20, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 59.20, 117.99, 121.78, 124.44, 127.56, 128.08, 128.15, 128.37, 129.00, 129.15, 131.36, 134.00, 134.18, 137.67, 148.75; MS (EI) *m/z* (%): 327 (3) [M^+], 251 (15), 173 (36), 156 (100), 77 (21); HRMS (EI): *m/z* calcd for $C_{17}H_{13}NO_4S$: 327.05653 [M^+]; found: 327.05576.

Reaction of 2-*tert*-butoxynitrobenzene with 1 (2 products)

(2-nitro-3-*tert*-butoxy)benzyl phenyl sulfone: yield 21%; m.p.169-170°C (EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.32 (s, 9H), 4.37 (s, 2H), 7.21 (dd, *J* = 8.10, *J* = 1.20, 1H), 7.27 (dd, *J* = 8.10, *J* = 1.20, 1H), 7.37 (t, *J* = 8.10, 1H), 7.45-7.50 (m, 2H), 7.61-7.68 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 28.84, 57.63, 82.71, 121.79, 123.53, 125.83, 128.59, 129.17, 130.41, 134.21, 137.50, 146.58, 148.48; MS (EI) *m/z* (%): 294 (15), 152 (100), 122 (10), 77 (23), 57 (52); HRMS (ESI): *m/z* calcd for $C_{17}H_{19}NO_5NaS$: 372.08762 [M^+]; found: 372.08612.

(4-nitro-3-*tert*-butoxy)benzyl phenyl sulfone: yield 17%; m.p. 129-131°C (EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.36 (s, 9H), 4.32 (s, 2H), 6.83 (dd, *J* = 8.25, *J* = 1.80, 1H), 7.05 (d, *J* = 1.80, 1H), 7.50-7.55 (m, 2H), 7.60 (d, *J* = 8.25, 1H), 7.62-7.71 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 28.71, 62.15, 83.33, 124.72, 124.86, 126.50, 128.48, 129.27, 133.24, 134.17, 137.55, 145.08, 149.21; MS (EI) *m/z* (%): 294

(27), 276 (8), 152 (96), 141 (19), 135 (36), 122 (33), 77 (63), 57 (100); HRMS (ESI): *m/z* calcd for $C_{17}H_{19}NO_5NaS$: 372.08762 [M^+]; found: 372.08617.

Reaction of 2-cyanonitrobenzene with 1 (2 products)

(3-cyano-2-nitro)benzyl phenyl sulfone: yield 52%; m.p. 194-195°C (hexane/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$): *d* = 4.42 (s, 2H), 7.56-7.60 (m, 2H), 7.61 (d, *J* = 1.87, 1H), 7.66 (dd, *J* = 8.53, *J* = 1.87, 1H), 7.72-7.75 (m, 3H), 8.28 (d, *J* = 8.53, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 61.35, 108.43, 114.14, 125.76, 128.42, 129.61, 134.82, 135.71, 135.85, 137.19, 137.41; MS (EI) *m/z* (%): 302 (6) [M^+], 141 (83), 131 (38), 115 (12), 77 (100), 51 (29); HRMS (EI): *m/z* calcd for $C_{14}H_{10}N_2O_4S$: 302.03613 [M^+]; found: 302.03584.

(3-cyano-4-nitro)benzyl phenyl sulfone: yield 43%; m.p. 180-182°C (hexane/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$): *d* = 4.70 (s, 2H), 7.53-7.58 (m, 2H), 7.69-7.75 (m, 4H), 7.82 (dd, *J* = 7.90, *J* = 1.55, 1H), 7.88 (dd, *J* = 7.9, *J* = 1.55, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 57.60, 108.66, 113.65, 123.98, 128.30, 129.63, 132.14, 134.14, 135.07, 137.34, 137.98, 151.19; MS (EI) *m/z* (%): 190 (1), 161 (63), 141 (42), 103 (20), 77 (100), 51 (23); HRMS (ESI): *m/z* calcd for $C_{14}H_{10}N_2O_4NaS$: 325.02535 [M^+]; found: 325.02548.

Reaction of 2-carboisopropoxynitrobenzene with 1 (2 products)

(3-carboisopropoxy-2-nitro)benzyl phenyl sulfone: yield 27%; m.p. 110-112°C (isopropanol); ^1H NMR (400 MHz, $CDCl_3$): *d* = 1.28 (d, *J* = 6.24, 6H), 4.46 (s, 2H), 5.16 (septet, *J*= 6.24, 1H), 7.49-7.54 (m, 2H), 7.60 (t, *J* = 7.85, 1H), 7.64-7.72 (m, 3H), 7.77 (dd, *J* = 7.85, *J* = 1.47, 1H), 7.94 (dd, *J* = 7.85, *J* = 1.47, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 21.25, 57.27, 70.76, 121.57, 126.00, 128.54, 129.37, 130.54, 131.55, 134.44, 136.04, 137.49, 162.86; MS (EI) *m/z* (%): 317 (7), 304 (15), 222 (68), 180 (100), 163 (36), 134 (17), 104 (28), 77 (45); HRMS (ESI): *m/z* calcd for $C_{17}H_{17}NO_6NaS$: 386.06688 [M^+]; found: 386.06617.

(3-carboisopropoxy-4-nitro)benzyl phenyl sulfone: yield 32%; m.p. 134-135°C (isopropanol); ^1H NMR (400 MHz, $CDCl_3$): *d* = 1.32 (d, *J* = 6.23, 6H), 4.39 (s, 2H), 5.22 (septet, *J* = 6.23, 1H), 7.36 (d, *J* = 2.02, 1H), 7.41 (dd, *J* = 8.34, *J* = 2.02, 1H), 7.51-7.57 (m, 2H), 7.65-7.72 (m, 3H), 7.82 (d, *J* = 8.34, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): *d* = 21.35, 61.77, 70.76, 124.08, 128.44, 128.55, 129.37, 132.08, 133.68, 133.72, 134.39, 137.27, 148.02, 164.01; MS (EI) *m/z* (%): 363 (1) [M^+], 321 (7), 304 (30), 222 (85), 163 (100), 133 (73), 106 (87), 89 (50), 77 (59), 63 (24), 51 (23); HRMS (EI): *m/z* calcd for $C_{17}H_{17}NO_6S$: 363.07766 [M^+]; found: 363.07588.

Reaction of 2,6-dichloronitrobenzene with 1 (1 product)

(3,5-dichloro-4-nitro)benzyl phenyl sulfone: yield 56%; m.p. 227-229°C (EtOH); ^1H NMR (400 MHz, $CDCl_3$): *d* = 4.27 (s, 2H), 7.21 (s, 2H), 7.56-7.62 (m, 2H), 7.70-7.73 (m, 1H), 7.74-7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 61.24, 126.65, 128.48, 129.51, 131.07, 132.36, 134.64, 137.26, 148.11; MS (EI) *m/z* (%): 345 (3) [M^+], 204 (30), 174 (28), 141 (100), 123 (29), 77 (84); HRMS (EI): *m/z* calcd for $C_{13}H_9NO_4SCl_2$: 344.96294 [M^+]; found: 344.96421.

Reaction of 2-chloro-4-trifluoromethylnitrobenzene with 1 (1 product)

(3-chloro-2-nitro-5-trifluoromethyl)benzyl phenyl sulfone: yield 88%; m.p. 165°C (EtOH); ^1H NMR (400 MHz, $CDCl_3$): *d* = 4.43 (s, 2H), 7.54-7.60 (m, 2H), 7.65 (br.s, 1H), 7.69-7.75 (m, 3H), 7.81 (br.s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 57.49, 121.87 (q, *J* = 273.71), 127.41, 128.20 (q, *J* = 3.45), 128.45, 128.75 (q, *J* = 3.45), 129.61, 133.30 (q, *J* = 34.92), 134.82, 137.15, 151.39; MS (EI) *m/z* (%): 314 (2), 238 (35), 221 (10), 141 (61), 77 (100), 51 (21); HRMS (ESI): *m/z* calcd for $C_{14}H_9NO_4F_3NaSCl$: 401.97851 [M^+]; found: 401.97833.

Preparative reaction ONSH of nitroarenes with *n*BuMgCl procedure.

To a solution of nitroarene (2.0 mmol) in THF (10 mL) cooled to -78°C a 1.5 mL 2 M solution of *n*-butylmagnesium chloride in THF (3 mmol) was added dropwise. After 5 min powdered $KMnO_4$ (0.4 g, 2.5 mmola) and liquid NH_3 (5 mL) was added and after 1 min the reaction mixture was treated with powdered NH_4Cl (0.5 g), then ammonia evaporated. Crude reaction mixture was treated with water, Na_2SO_3 to the decolourization and aqueous HCl (1:10), extracted with CH_2Cl_2 (100 mL), washed with water. Extracts were dried with $MgSO_4$, products were isolated and purified by column chromatography.

Spectral data of product formed in ONSH reaction

The most products of ONSH reaction with chloromethyl phenyl sulfone is described in the literature.[4]

2-*n*butyl-4-cyano-1-nitrobenzene: yield: 67%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 0.96 (t, *J* = 7.32, 3H); 1.42-1.46 (m, 2H), 1.60-1.66 (m, 2H), 2.86-2.91 (m, 2H), 7.65 (dd, *J* = 8.24, *J* = 1.83, 1H), 7.68 (dd, *J* = 1.83, *J* = 0.46, 1H), 7.92 (d, *J* = 8.24, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 13.68, 22.51, 32.08, 32.43, 116.37, 116.97, 125.09, 130.49, 135.62, 138.72, 151.69; MS (EI) *m/z* (%): 204 (9) [M^+], 187 (100), 169 (24), 145 (63), 117 (40), 102 (36), 90 (35), 43 (30); HRMS (EI): *m/z* calcd for $C_{11}H_{12}O_2N_2$: 204.08988 [M^+]; found: 204.09008.

Calculation of total relative activities of competing nitroarenes

A_0 - starting concentration of nitroarene A

B_0 - starting concentration of nitroarene B

A - final concentration of nitroarene A

B - final concentration of nitroarene B

P_A - final concentration of product(s) formed from nitroarene A

P_B - final concentration of product(s) formed from nitroarene B

C - final concentration of carbanion

S - conversion of sulfone **1**

k_A - relative rate constant of the addition of carbanion to nitroarene A

k_B - relative rate constant of the addition of carbanion to nitroarene B

y_A - yield of the product(s) formed from nitroarene A, determined by GLC analysis using internal standard

y_B - yield of the product(s) formed from nitroarene B, determined b GLC analysis using internal standard

Final concentration of nitroarene A and B can be described by the equations:

$$A = A_0 - P_A$$

$$B = B_0 - P_B$$

Equations describing rates of competing reactions:

$$\frac{dP_A}{dt} = -\frac{dA}{dt} = k_A \cdot A \cdot C$$

$$\frac{dP_B}{dt} = -\frac{dB}{dt} = k_B \cdot B \cdot C$$

Dividing above equations:

$$\frac{dP_A}{dP_B} = \frac{k_A \cdot A \cdot C}{k_B \cdot B \cdot C} = \frac{k_A}{k_B} \cdot \left(\frac{A_0 - P_A}{B_0 - P_B} \right) \qquad \cdot / \left(\frac{dP_B}{A_0 - P_A} \right)$$

$$\frac{dP_A}{(A_0 - P_A)} = \frac{k_A}{k_B} \cdot \frac{dP_B}{(B_0 - P_B)}$$

After taking into account the solution of the integral:

$$\ln\left(\frac{A_0 - P_A}{P_A} \right) = \frac{k_A}{k_B} \cdot \ln\left(\frac{B_0 - P_B}{P_B} \right)$$

$$\frac{k_B}{k_A} = \frac{\ln\left(\frac{B_0 - P_B}{B_0} \right)}{\ln\left(\frac{A_0 - P_A}{A_0} \right)} \qquad [i]$$

where:

$$P_A = \frac{y_A \cdot S}{y_A + y_B} = \frac{S}{1 + \left(\frac{y_B}{y_A} \right)}$$

$$P_B = S - P_A$$

Calculation of partial relative activities of various positions in competing nitroarenes

On the basis of one example we show the calculation of ratios of rate constans for *ortho* and *para* substitution, which were then re-calculated to obtain relative activities reffered to that of the one *ortho* position in nitrobenzene, equals 1.

Numerals in parenthesis, e.g. (4-) means position „4” in nitroarene.

Term $\binom{4-}{2-}_A$ means ratio of amounts of isomer 4- to isomer 2- in nitroarene A; otherwise: $\frac{k_A^{(4-)}}{k_A^{(2-)}}$. $k_A^{(4-)}$ means rate constant of the reaction (addition) of carbanion with nitroarene A in position 4-.

Version: A = *o*-Z$_1$-nitrobenzene i B = *o*-Z$_2$-nitrobenzene

$$\frac{k_A^{(4-)}}{k_A^{(2-)}} = \binom{4-}{2-}_A \qquad => \qquad k_A^{(4-)} = \binom{4-}{2-}_A \cdot k_A^{(2-)} \qquad [ii]$$

$$\frac{k_B^{(4-)}}{k_B^{(2-)}} = \binom{4-}{2-}_B \qquad => \qquad k_B^{(4-)} = \binom{4-}{2-}_B \cdot k_B^{(2-)} \qquad [iii]$$

Total rate constant of reaction A (or B) with carbanion is the sum of rates of formation isomers 4- and 2-:

$$k_A^{(4-)+(2-)} = k_A^{(4-)} + k_A^{(2-)} \qquad [iv]$$

$$k_B^{(4-)+(2-)} = k_B^{(4-)} + k_B^{(2-)} \qquad [v]$$

After substitution of eq. [ii] and [iii] to [iv] and [v]:

$$k_A^{(4-)+(2-)} = k_A^{(2-)} + \binom{4-}{2-}_A \cdot k_A^{(2-)}$$

$$k_B^{(4-)+(2-)} = k_B^{(2-)} + \binom{4-}{2-}_B \cdot k_B^{(2-)}$$

The result of division is eq.[vi]:

$$\frac{k_A^{(4-)+(2-)}}{k_B^{(4-)+(2-)}} = \frac{k_A^{(2-)}}{k_B^{(2-)}} \cdot \frac{1+\binom{4-}{2-}_A}{1+\binom{4-}{2-}_B} \qquad [vi]$$

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(4-)+(2-)}}{k_A^{(4-)+(2-)}} \cdot \frac{1+\binom{4-}{2-}_A}{1+\binom{4-}{2-}_B}$$

Term $\frac{k_B^{(4-)+(2-)}}{k_A^{(4-)+(2-)}}$ equals $\frac{k_B}{k_A}$ calculated from eq. [i].

$\frac{k_B^{(2-)}}{k_A^{(2-)}}$ can be calculated from known ratio of total rate constants of addition to A and B and ratio of isomer 4- to isomer 2- in nitroarene A and B.

Then from the simple calculation the wanted relations can be determined.

$$\frac{k_A^{(4-)}}{k_B^{(2-)}} = \frac{k_A^{(2-)}}{k_B^{(2-)}} \cdot \left(\tfrac{4-}{2-}\right)_A$$

Version: A = *p*-Z$_1$-nitrobenzene and B = *o*-Z$_2$-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(4-)+(2-)}}{k_A^{(6-)+(2-)}} \cdot \frac{2}{1+\left(\tfrac{4-}{2-}\right)_B}$$

Version: A = *o*-Z$_1$-nitrobenzene and B = *m*-Z$_2$-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(4-)+(2-)+(6-)}}{k_A^{(4-)+(2-)}} \cdot \frac{1+\left(\tfrac{4-}{2-}\right)_A}{1+\left(\tfrac{4-}{2-}\right)_B+\left(\tfrac{6-}{2-}\right)_A}$$

Version: A = nitrobenzene and B = *o*-Z-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(4-)+(2-)+(6-)}}{k_A^{(4-)+(2-)+(6-)}} \cdot \frac{2+\left(\tfrac{4-}{2-}\right)_A}{1+\left(\tfrac{4-}{2-}\right)_B}$$

Version: A = nitrobenzene and B = *p*-Z-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(2-)+(6-)}}{k_A^{(4-)+(2-)+(6-)}} \cdot \frac{2+\left(\tfrac{4-}{2-}\right)_A}{2}$$

Version: A = nitrobenzene and B = *m*-Z-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(4-)+(2-)+(6-)}}{k_A^{(4-)+(2-)+(6-)}} \cdot \frac{2+\left(\tfrac{4-}{2-}\right)_A}{1+\left(\tfrac{4-}{2-}\right)_B+\left(\tfrac{6-}{2-}\right)_B}$$

Version: A = *p*-Z$_1$-nitrobenzene and B = *p*-Z$_2$-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(2-)+(6-)}}{k_A^{(2-)+(6-)}}$$

Version: A = *p*-Z_1-nitrobenzene and B = *m*-Z_2-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(4-)+(2-)+(6-)}}{k_A^{(2-)+(6-)}} \cdot \frac{2}{1+\binom{4-}{2-}_B+\binom{6-}{2-}_B}$$

Version: A = *m*-Z_1-nitrobenzene and B = *m*-Z_2-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(4-)+(2-)+(6-)}}{k_A^{(4-)+(2-)+(6-)}} \cdot \frac{1+\binom{4-}{2-}_A+\binom{6-}{2-}_A}{1+\binom{4-}{2-}_B+\binom{6-}{2-}_B}$$

Version: A = 2,4-diZ_1-nitrobenzene and B = *o*-Z_2-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(4-)+(6-)}}{k_A^{(6-)}} \cdot \frac{1}{1+\binom{4-}{2-}_B}$$

Version: A = 2,4-diZ_1-nitrobenzene and B = *p*-Z_2-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(2-)+(6-)}}{k_A^{(6-)}} \cdot \frac{1}{2}$$

Version: A = 2,4-diZ_1-nitrobenzene and B = *m*-Z_2-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(4-)+(2-)+(6-)}}{k_A^{(6-)}} \cdot \frac{1}{1+\binom{4-}{2-}_B+\binom{6-}{2-}_B}$$

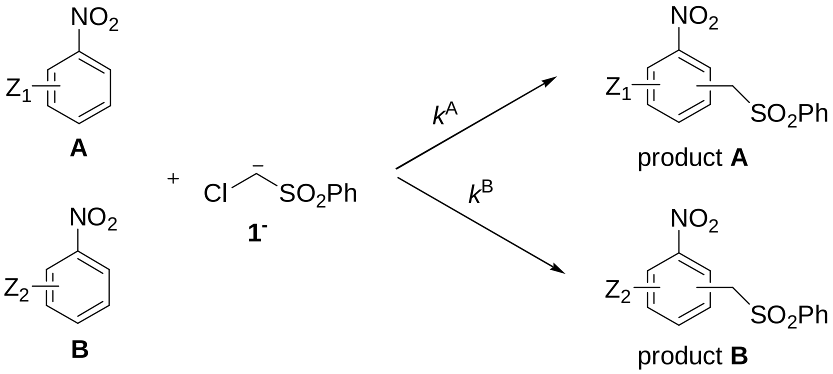
Version: A = 2,4-diZ_1-nitrobenzene and B = 2,4-diZ_2-nitrobenzene

$$\frac{k_B^{(2-)}}{k_A^{(2-)}} = \frac{k_B^{(6-)}}{k_A^{(6-)}}$$

2,6-disubstituted nitroarenes in which reaction proceeds only in 4- position, should be treated as 2,4-disubstituted. 2,6-disubstituted nitrobenzene forming two products, in positions 2- and 4-, shoud be treated as *ortho*-substituted nitroarene.

meta-Z-nitrobenzene giving only two isomers should be treated as *ortho*-substituted nitrobenzene; analogously – only one isomer – as 2,4-disubstituted nitroarene.

Results of competitive experiments



Scheme 1. Competition between nitroarene A and B with carbanion **1^-.**

Table 1. Results of competitive experiment of VNS reactions for *para*-substitited nitroarenes, according to Scheme 1

No	Nitroarene A Z_1	Nitroarene B Z_2	k^B / k^A (competing positions)	Standard deviation [%]
1	H	4-*t*Bu	0.36 (2-/2-)	2.7
2	H	4-MeO	0.92 (2-/2-)	0.74
3	H	4-PhO	2.7 (2-/2-)	3.9
4	H	4-Cl	130 (2-/2-)[a]	1.3
5	2-Cl	4-Cl	14 (2-/6-)[a] 13 (2-/4-)[a]	2.6
6	4-Cl	4-Br	1.2 (2-/2-)[a]	0.83
7	4-*i*Pr	4-MeO	3.1 (2-/2-)	2.6
8	4-MeO	4-tBu	0.42 (2-/2-)	0.82
9	4-MeO	4-$CH(OCH_2)_2$	1.0 (2-/2-)	1.7
10	4-F	4-Cl	2.5 (2-/2-)	1.1
11	4-MeS	4-MeO	4.2 (2-/2-)	3.9
12	4-PhS	4-Cl	10.8 (2-/2-)	2.5
13	4-I	4-Cl	2.8 (2-/2-)	2.9

14	4-COO-*i*Pr	4-Cl	7.3 (2-/2-)	3.7
15	4-COO-*i*Pr	4-F	3.7 (2-/2-)	-[b]
16	4-CF$_3$	2,4-Cl$_2$	1.1 (2-/2-)	1.1
17	4-Cl	4-CN	8.5 (2-/2-)	4.8
18	2,4-Cl$_2$	1-nitronaphthalene	6.6 (2-/2-)	2.1
19	4-CF$_3$	1-nitronaphthalene	6.7 (2-/2-)	0.4

[a] Results in agreement with data published earlier.[5]

[b] Only one experiment was made.

Table 2. Results of competitive experiment of VNS reactions for *ortho*-substituted nitroarenes, according to Scheme 1.

No	Nitroarene A Z$_1$	Nitroarene B Z$_2$	k^B/ k^A (competing positions)	Standard deviation [%]
1	H	-	1.4 (2-/4-)[a]	1.0
5	H	2-Cl	8.5 (6-/2-)[a]	5.6
			8.8 (4-/2-)[a]	
6	2-Cl	2-Br	0.80 (6-/6-)[a]	5.4
			0.72 (4-/6-)[a]	
7	2-F	4-Cl	5.7 (2-/2-)	7.9
			5.9 (2-/6-)	
			5.2 (2-/4-)	
8	2-I	4-MeO	No product of A reaction	-
9	4-Cl	2-CN	14 (6-/2-)	6.7
			9.3 (4-/2-)	
10	2-COO-*i*Pr	4-Cl	8.6 (2-/6-)	9.4
			13 (2-/4-)	
11	4-Cl	2-CF$_3$	0.93 (2-/2-)	3.5
			0.49 (4-/2-)	

[a] Results in agreement with data published earlier.[5]

Table 3. Results of competitive experiment of VNS reactions for disubstituted nitroarenes, according to Scheme 1.

Nr	Nitroarene A Z$_1$	Nitroarene B Z$_2$	k^B/ k^A (competing positions)	Standard deviation [%]
1	2-Cl	2,4-Cl$_2$	75 (6-/6-)[a]	1.6
2	4-Cl	2,4-Cl$_2$	6.2 (6-/2-)[a]	2.2
3	2,4-Cl$_2$	2-Cl,4-CF$_3$	5.2 (6-/6-)	7.2
4	2,4-F$_2$	2,4-Cl$_2$	1.0 (6-/2-)	6.0
			1.7 (6-/6-)	
5	2,6-Cl$_2$	4-MeO	1.4 (2-/4-)	1.9

6	2-MeO,5-NO_2	3-CN	1.5 (2-+4-+6-/4-)	2.3
7	2,6-F_2	4-Cl	1.2 (2-/2-)	4.9
			0.86 (2-/4-)	

[a] Results in agreement with data published earlier.[5]

Table 4. Results of competitive experiment of VNS reactions for *meta*-substituted nitroarenes, according to Scheme 1.

No	Nitroarene A Z_1	Nitroarene B Z_2	k^B/ k^A (competing positions)	Standard deviation [%]
1	4-Cl	3-Cl	4.7 (2-/2-)	3.0
			0.85 (6-/2-)	
2	4-Cl	3-Br	2.9 (2-/2-)	0.63
			0.69 (6-/2-)	
3	4-Cl	3-I	0.50 (2-/2-)	4.6
			0.16 (6-/2-)	
4	4-Cl	3-F	0.14 (2-/2-)	5.8
			0.026 (6-/2-)	
			0.21 (4-/2-)	
5	2-Cl, 4-CF_3	3-CN	1.2 (2-/6-)	2.3
			0.35 (6-/6-)	
			2.7 (4-/6-)	
6	4-Cl	3-COOMe	31 (6-/2-)	3.4
			7.8 (4-/2-)	
7	4-PhO	3-MeO	0.23 (2-/2-)	7.0
			0.078 (6-/2-)	
			0.83 (4-/2-)	
8	4-*t*Bu	3-Me	1.0 (2-/2-)	5.0
			0.52 (6-/2-)	
			1.7 (4-/2-)	
9	2,4-Cl_2	3-CF_3	7.0 (6-/6-)	4.3

Table 5. Data used for construction of plot on Fig. 6 in main text of the paper.

No	Nitroarene, Z	s_m[6]	k_Z/ k_0	log k_Z/ k_0
1	4-*t*Bu	-0.09	0.36	-0.44
2	4-*i*Pr	-0.08	0.29	-0.54
3	H	0	1	0.00
4	4-MeO	0.1	0.89	-0.05
5	4-MeS	0.14	11	1.04
6	4-PhO	0.25	2.7	0.43

7	4-F	0.34	50	1.70
8	4-I	0.34	44	1.64
9	4-COO-*i*Pr	0.35	15	1.18
10	4-Cl	0.37	125	2.10
11	4-Br	0.37	145	2.16
12	4-CF_3	0.46	640	2.81
13	4-CN	0.62	1050	3.02

Results of relative activities of nitroarenes calculated on the basis of more than one competitive experiment of VNS reactions.

Table 6.

No	Nitroarene, Z	**1**	
		partial	overall
1	4-*i*Pr	2- 0.28-0.30	0.56-0.60
2	4-*t*Bu	2- 0.36	0.72
3	3-Me	2- 0.36 4- 0.61 6- 0.19	1.2
4	2,6-Cl_2	4- 1.2-1.3	1.2-1.3
5	4-MeO	2- 0.85-0.92	1.7-1.8
6	4-$CH(OCH_2)_2$	2- 0.87-0.97	1.7-1.9
7	H	2- 1.0 4- 0.70	2.7
8	3-MeO	2- 0.62 4- 2.2 6- 0.21	3.0
9	4-PhO	2- 2.7	5.4
10	4-MeS	2- 3.8	7.6
11	2-Br	4- 6.2 6- 6.9	13
12	2-Cl	4- 8.8 6- 8.6	17
13	4-PhS	2- 11-12	22-24
14	2-COO*i*Pr	4- 9.3-10 6- 14-15	23-25
15	4-COO*i*Pr	2- 13-18	26-36
16	3-F	2- 17-18 4- 25-27 6- 3.1-3.4	45-48
17	2-F	2- 21-23 4- 23-25 6- 20-22	64-70
18	3-I	2- 60-65 6- 19-21	79-86
19	4-I	2- 43-46	86-92

20	4-F	2- 48-52	96-100
21	2-CF_3	2- 110-120 4- 59-64	170-180
22	4-Cl	2- 120-130	240-260
23	4-Br	2- 140-150	280-300
24	2,6-F_2	2- 100-110 4- 140-150	340-370
25	3-Br	2- 350-380 6- 83-90	430-470
26	3-Cl	2- 560-610 6- 100-110	660-720
27	2,4-Cl_2	6- 640-780	640-780
28	2,4-F_2	2- 620-760 6- 370-460	990-1200
29	4-CF_3	2- 580-700	1200-1400
30	4-CN	2- 1000-1100	2000-2200
31	2-CN	4- 1100-1200 6- 1600-1800	2700-3000
32	2-Cl-4-CF_3	6- 3300-4100	3300-4100
33	1-nitronaphthalene	2- 3900-5200	3900-5200
34	3-COOMe	4- 940-1000 6- 3800-4000	4700-5000
35	3-CF_3	6- 4500-5400	4500-5400
36	3-NO_2,4-MeO	6- 8000-10000	9000
37	3-CN	2- 3100-4900 4- 9000-11000 6- 1200-1400	13000-17000

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