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Oxidative nucleophilic substitution of hydrogen in nitroarenes by silyl enol ethers

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Abstract—Enolates generated by treatment of silyl ketene acetals and enol ethers with fluoride ion sources add to nitroarenes to produce σ^H adducts that oxidize either with $KMnO_4$ to give substituted nitroarenes or with dimethyldioxirane to give substituted phenols. In the latter case the oxidation results in replacement of the nitro group with a hydroxy group. It was shown that high effectiveness of these reactions is not due to stabilization of the σ^H adducts via O-silylation but due to the nature of the accompanying cation.

1. Introduction

In our previous papers[1,2] we have reported that in the addition of the 2-phenylpropionitrile carbanion to nitrobenzene and its derivatives the equilibrium is shifted to the σ^H adducts and that these adducts are efficiently oxidized by external oxidants such as $KMnO_4$ in liquid ammonia (pathway a in Scheme 1) and dimethyldioxirane (DMD) in acetone (pathway b in Scheme 1). These two oxidants gave different products leading to an assumption that they react with the σ^H adducts at different places. Permanganate anion presumably attacks the σ^H adduct at the addition site of the nucleophile, producing substituted nitroarenes—products of oxidative nucleophilic substitution of hydrogen (ONSH),[1] whereas oxidation with DMD proceeds at the carbon bearing the nitro group giving substituted phenols.[2]

It was also observed that treatment of this σ^H adduct with Me_3SiCl gave a substituted nitroso compound, apparently via silylation of the nitro group followed by elimination of silanol (pathway c in Scheme 1).[3] This reaction is similar to that observed when σ^H adducts of the Grignard reagents are treated with strong acids[4] and can be considered as an intramolecular redox process.

The σ^H adducts can also be generated by reaction of nitroarenes with silyl acetals of ketenes or silyl enol ethers in the presence of fluoride ion, usually provided by tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF).[5] These σ^H adducts may be oxidized with DDQ or Br_2 to give nitroarylated esters or ketones the products of ONSH. High yields were rationalized in term of stabilization of the σ^H adducts via silylation. The aim of this study was to verify that supposition and to explore other oxidative transformations of the respective σ^H adducts.

2. Results and discussion

The reaction of silyl ketene acetal **5a** with nitrobenzenes **4a–d** were carried out in the presence of an equivalent of TASF in THF and then the resulting σ^H adducts were oxidized with $KMnO_4$ in liquid ammonia.[6] The expected products of ONSH were formed in good yield. When DMD in acetone was used for oxidation of the σ^H adducts, substituted phenols were the main products accompanied with some amounts of substituted nitro compounds, products of ONSH (Scheme 2).

Treatment of **5a** and nitroanisole with TASF under the same conditions resulted in recovery of the nitroarene suggesting that nucleophilic addition to this less electrophilic arene is unfavorable.

It is know that the bulky enolate of **5a** added to nitrobenzene in the *para* position whereas addition of ethyl trimethylsilylacetate **5b** occur *ortho* to the nitro group predominately.[5b] To avoid formation of products mixtures we studied the reaction of **5b** with *p*-chloronitrobenzene **4e**. The σ^H adduct produced when **5b** and **4e** were treated with TASF was efficiently oxidized with DMD giving ethyl (5-chloro-2-hydroxyphenyl)acetate **8b** in 62% yield. Oxidation with $KMnO_4$ in liquid NH_3 was less satisfactory giving the expected ONSH product **8a** in low yield (Scheme 3). Apparently the product **8a**, being a strong CH acid, is deprotonated and further oxidized. It was observed

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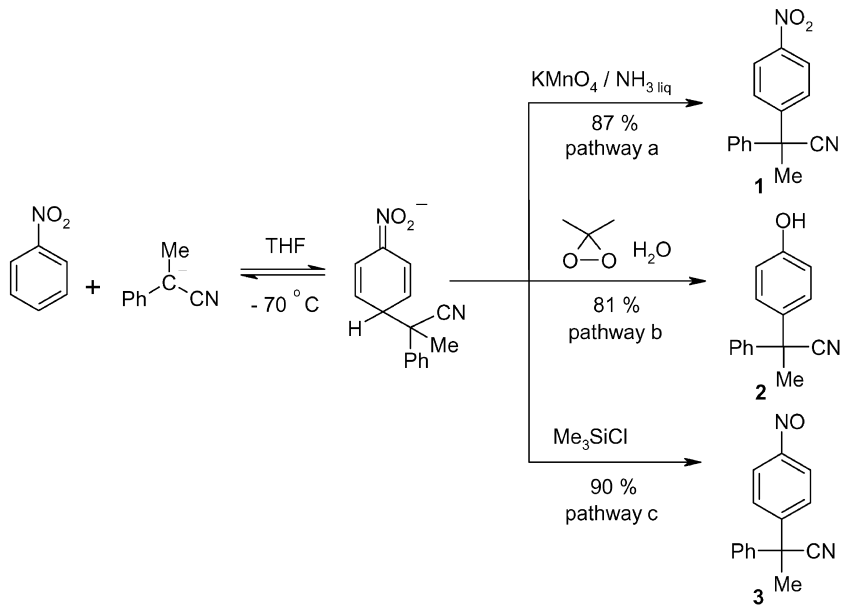


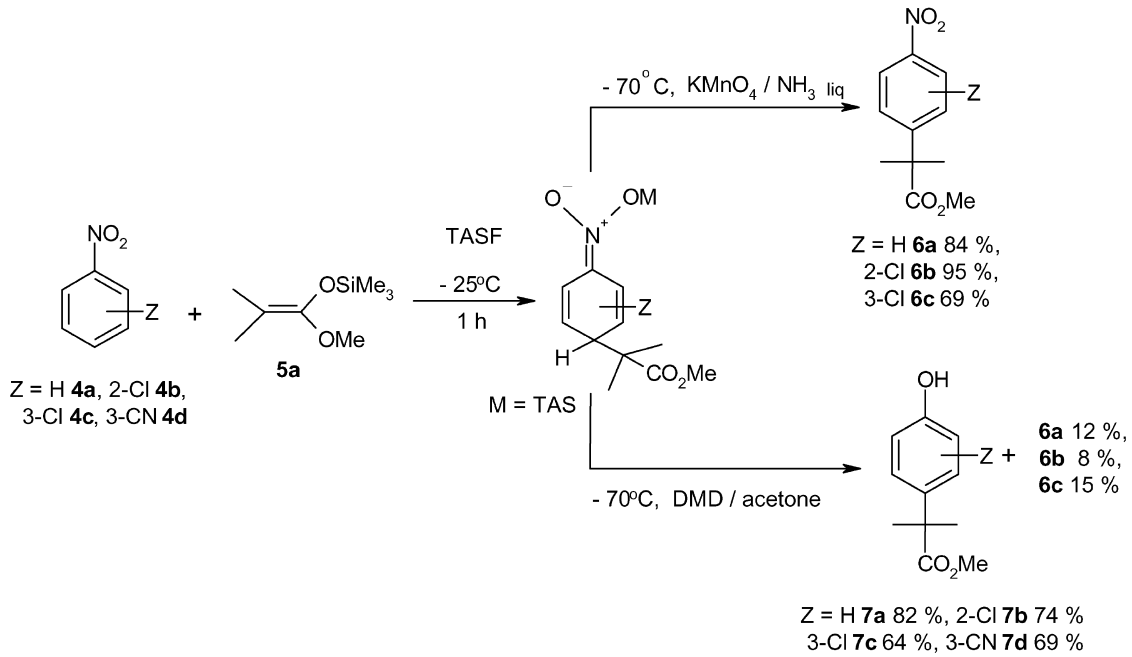
Scheme 1.

earlier that oxidation of the σ^H adducts of phenylacetonitrile to nitrobenzenes with $KMnO_4$ in liquid ammonia gave *ortho*- and *para*-nitrobenzophenones,[1e,3] whereas the analogous reaction with 2-phenylpropionitrile gave ONSH products in high yields.[1]

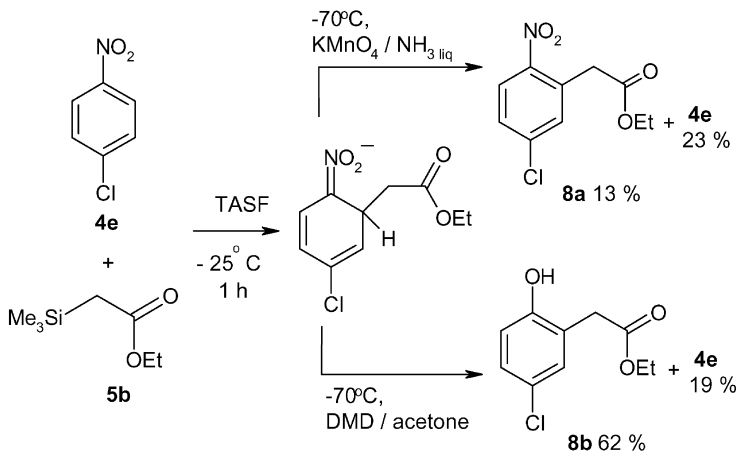
Ketone enolates generated by treatment of silyl enol ethers with TASF are apparently weaker nucleophiles so addition to nitroarenes is less efficient, e.g. it was reported that the reactions of **5c** with chloronitrobenzenes gave the ONSH products in yield 30–50%.[5b] Also in our hands the TASF promoted addition of **5c** to *m*-chloronitrobenzene **4c** followed by oxidation with DMD gave expected 2-(2-chloro-4-hydroxyphenyl)cyclohexanone in moderate yield 21%, majority of the starting nitroarene **4c** 61% was recovered (Scheme 4).

Due to the high price of TASF and its sensitivity to moisture, we looked for a more convenient source of fluoride to promote the reactions of silylated enols with nitroarenes. We have found that readily available Bu_4N^+ $(p\text{-tolyl})_3SiF_2^-$ **9**[7] is almost as efficient as TASF in this respect. The reaction of **4a** with **5a** promoted by **9** gave **7a** in 72% yield after oxidation with DMD.

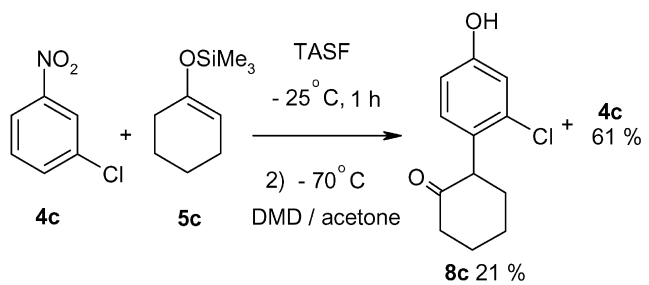
The efficiency of TASF promoted reactions between silylated enols and nitroarenes was provisionally rationalized in terms of stabilization of the σ^H adducts by



Scheme 2.



Scheme 3.



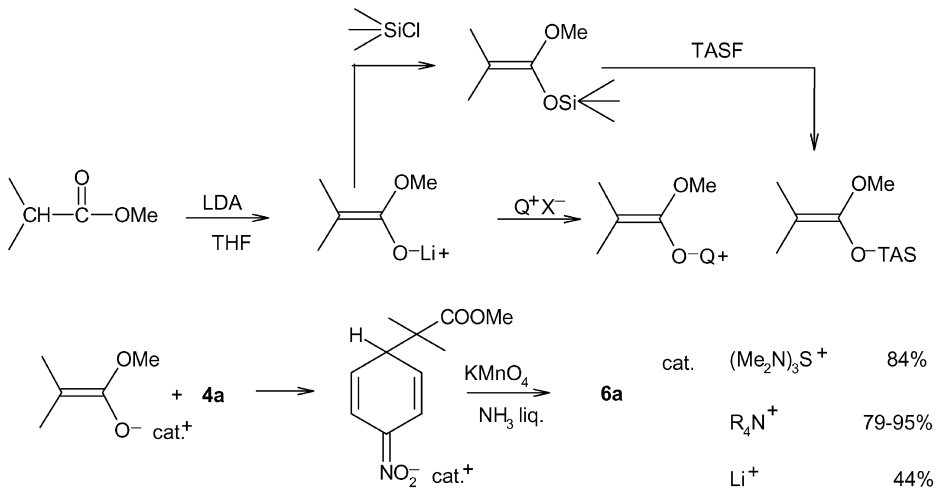
Scheme 4.

O-silylation.[5] This is however in contradiction to the experimental observation that a stoichiometric amount of fluoride ion is needed for the reaction whereas in the fluoride promoted reactions of trimethylsilyl enol ethers with aldehydes where O-silylation takes place, only a catalytic amount of fluoride ion is needed.[8] Moreover silylation of the σ^H adducts of the 2-phenylpropionitrile carbanion gave substituted nitrosoarenes (Scheme 1, path c).

In order to clarify whether σ^H adducts can indeed be stabilized by O-silylation a mixture of 2-phenylpropionitrile carbanion and nitrobenzene was treated with Me_3SiCl and subsequently with DMD. The sole product of this reaction was the substituted nitrobenzene **1**, the product of ONSH, whereas the same reaction without Me_3SiCl gave substituted phenol **2**. Analogous results were obtained in the TASF promoted reaction of **5a** with nitrobenzene. Treatment of the σ^H adduct with Me_3SiCl and subsequent oxidation with DMD gave the ONSH product **6a** whereas its direct oxidation with DMD gave phenol **7a** as the main product. These results indicate unambiguously that O-silylation of the σ^H adducts is followed by rapid elimination of silanol and formation of the nitroso compounds that are further oxidized with DMD to the nitro compounds. Thus the σ^H adducts of enolates produced via treatment of silylated enols with TASF are not stabilized by O-silylation.

It is well known that nucleophilicity of anions depends very much on cation–anion interactions. Also oxidation of the anionic σ^H adducts is affected by the counter cations.[9] One can therefore suppose that high effectiveness of the TASF promoted reactions can be due to a nature of cation associated with the enolate and subsequently the σ^H adducts.

Direct comparison of the reaction of the enolates generated by treatment of **5a** with TASF, deprotonation of methyl *iso*-butyrate with LDA and that produced via exchange of Li^+ for tetraalkylammonium cation, Q^+ in the latter, revealed that the results are strongly affected by the nature of the



Scheme 5.

Table 1. ONSH in nitrobenzene with lithium and tetraalkyl ammonium salts of methyl isobutyrate carbanion (as in Scheme 5)

Ammonium salt	Composition of the reaction mixture (%)	
	6a	**4a**
$Bu_4N^+BF_4^-$	79	18
$Bu_4N^+Br^-$	84	14
$(PhCH_2)Et_3N^+Cl^-$	95	3

cation (Scheme 5). As it is shown in the Table 1 the reaction of tetraalkyl ammonium salts of enolates with nitrobenzene proceeds much better than the lithium salt and even better than the tris(dimethylamino)sulfonium salt (Scheme 5).

3. Conclusion

We have found that σ^H adducts produced via TASF promoted addition of enolates to nitrobenzenes are efficiently oxidized by $KMnO_4$ to form substituted nitroarenes, products of ONSH and by DMD to form substituted phenols. High effectiveness of these reaction is due to the type of counter ion: tris(dimethylamino)sulfonium cation. Silylation of the σ^H adducts does not proceed in these processes. We have also shown that reaction of lithium enolates with nitrobenzenes proceeds better upon exchange of the lithium for a tetraalkylammonium cation. This protocol offers substantial advantages over the analogous reaction of silyl enol ethers in the presence of stoichiometric amounts of TASF.

4. Experimental

4.1. General methods

Melting points are uncorrected. Infrared spectra were recorded on a Spectrum 2000 spectrometer, solids as Nujol mulls and liquids as thin films. ^1H and ^{13}C NMR spectra were measured at 400 MHz on a Mercury-400BB spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane as internal standard. Mass spectra were obtained on AMD 604 Inectra GmbH spectrometer using EI. Appropriate isotope patterns were observed. For analytical TLC Merck alufolien sheets Kieselgel 60 F_{254} while for preparative TLC Lachema silica gel was used. Solvents and reagents were used commercially except for tetrahydrofuran that was distilled over potassium benzophenone ketyl before use.

Acetone solution of DMD was prepared according to the procedure described by Adam.[10]

Starting materials were commercial products. Silyl enol ethers were prepared according to the standard procedures: 1-methoxy-2-methyl-1-trimethylsiloxypropene (**5a**)[11], ethyl trimethyl-silylacetate (**5b**)[12], 1-(trimethylsiloxy)cyclohexene (**5c**)[13].

4.2. General procedure for the reactions of silyl enol ethers with nitroarenes

To a stirred solution of silyl enol ether **5a–c** (0.5 mmol) and nitroarene **4a–e** (0.5 mmol) in THF (5 mL) at −70°C under argon, TASF (153 mg, 0.5 mmol) dissolved in MeCN (1 mL) was added dropwise and the mixture was placed in cooling bath −25°C for 1 h. After that the mixture was again cooled to −70°C and oxidant was added.

Procedure A. Powdered $KMnO_4$ (80 mg, 0.5 mmol) and liquid ammonia (ca. 5 mL, −70°C) was added, the reaction mixture was stirred for 15 min. and treated with NH_4Cl (106 mg, 2 mmol). The cooling bath was removed and the ammonia was evaporated. To the residue a saturated solution of oxalic acid in aq. HCl (20 mL, 10%) was added and the mixture was extracted with CH_2Cl_2 (4×10 mL). The combined organic layers were dried over $MgSO_4$, filtered through silica gel and the solvent was evaporated (25°C, 15 Torr).

Procedure B. Water (9 μL, 0.5 mmol) and than an acetone solution of DMD (ca. 0.6 mmol, 10 mL of ca. 0.06 M) was added to the mixture. The color changed to bright yellow. After 5 min of further stirring, saturated aqueous NH_4Cl (0.1 mL) was added and the cooling bath was removed. The solution was dried over anhydrous $MgSO_4$, the solid phase was filtered off and washed with acetone (20 mL). The solvents were evaporated (25°C, 15 Torr).

The products were purified by column chromatography on silica gel or by preparative TLC with hexane/ethyl acetate as an eluent.

4.2.1. Methyl 2-(4-nitrophenyl)-2-methylpropionate (6a). *Procedure A*. Yield 93 mg, 84%, light yellow oil (lit.[5b] oil). ^1H NMR (400 MHz, $CDCl_3$): 8.21–8.16 (m, 2H), 7.53–7.48 (m, 2H), 3.68 (s, 3H), 1.63 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 176.0, 151.9, 146.7, 126.8, 123.6, 52.5, 46.9, 26.4. IR (KBr): 3111, 3006, 2976, 2955, 1730, 1604, 1597, 1519, 1438, 1392, 1347, 1263, 1197, 1156, 1095, 860, 854, 739, 698. Anal. calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.27; H, 5.83; N, 6.25.

4.2.2. Methyl 2-(4-hydroxyphenyl)-2-methylpropionate (7a). *Procedure B*. Yield 80 mg, 82%, pale yellow crystals mp 104–105°C (EtOH), (lit.[14] 91–94°C). ^1H NMR (400 MHz, $CDCl_3$): 7.22–7.16 (m, 2H), 6.81–6.74 (m, 2H), 5.83 (s broad, 1H), 3.66 (s, 3H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 178.0, 154.5, 136.4, 126.9, 115.2, 52.3, 45.8, 26.5. IR (KBr): 3367, 3031, 2990, 2976, 2957, 2942, 2879, 1879, 1698, 1612, 1595, 1516, 1471, 1438, 1368, 1277, 1218, 1205, 1180, 1155, 1097, 974, 827, 779, 657, 546. Anal. calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.92; H, 7.34.

4.2.3. Methyl 2-(3-chloro-4-nitrophenyl)-2-methylpropionate (6b). *Procedure A*. Yield 123 mg, 95%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 7.87 (d, 1H, J=8.6 Hz), 7.53 (d, 1H, J=2.1 Hz), 7.40 (dd, 1H, J=8.6, 2.1 Hz), 3.70 (s, 3H), 1.62 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 175.4, 150.8, 146.1, 129.4 127.1, 125.6, 125.3, 52.6, 49.6, 26.1. Anal. calcd for $C_{11}H_{12}NO_4Cl$: C, 51.27; H, 4.69; N, 5.44. Found: C, 51.52; H, 4.62; N, 5.55.

4.2.4. Methyl 2-(3-chloro-4-hydroxyphenyl)-2-methylpropionate (7b). *Procedure B*. Yield 85 mg, 74%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.30 (d, 1H, *J*=2.4 Hz), 7.14 (dd, 1H, *J*=8.6, 2.4 Hz), 6.94 (d, 1H, *J*=8.6 Hz), 3.66 (s, 3H), 1.55 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 176.9, 150.1, 137.8, 126.4, 125.9, 119.7, 116.0, 52.3, 45.7, 26.4. EIMS(+) 230 (7.2), 228 (21.9), 171 (32.6), 169 (100.0), 141 (13.6). HR EIMS calcd for $C_{11}H_{13}O_3^{35}Cl$ M=228.0553. Found: 228.0559.

4.2.5. Methyl 2-(2-chloro-4-nitrophenyl)-2-methylopropionate (6c). *Procedure A*. Yield 89 mg, 69%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.23 (d, 1H, *J*=2.4 Hz), 8.14 (dd, 1H, *J*=8.7, 2.4 Hz), 7.63 (d, 1H, *J*=8.7 Hz), 3.69 (s, 3H), 1.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 175.9, 149.4, 146.9, 134.6, 127.6, 125.5, 121.8, 52.6, 47.0, 25.7. Anal. calcd for $C_{11}H_{12}NO_4Cl$: C, 51.27; H, 4.69; N, 5.44. Found: C, 51.43; H, 4.80; N, 5.31.

4.2.6. Methyl 2-(2-chloro-4-hydroxyphenyl)-2-methylopropionate (7c). *Procedure B*. Yield 74 mg, 64%, orange oil (lit.[15] oil). ^{1}H NMR (400 MHz, $CDCl_3$): 7.23 (d, 1H, *J*=8.6 Hz), 6.98 (s broad, 1H), 6.84 (d, 1H, *J*=2.6 Hz), 6.71 (dd, 1H, *J*=8.6, 2.6 Hz), 3.74 (s, 3H), 1.61 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 179.0, 155.4, 133.6, 127.4, 125.3, 117.8, 114.0, 52.7, 46.2, 26.2. EIMS(+) 230 (6.23), 228 (17.2), 193 (50.4), 171 (33.3), 169 (100.0), 143 (16.6), 141 (48.6). HR EIMS calcd for $C_{11}H_{13}O_3^{35}Cl$ M=228.0553. Found: 228.0558.

4.2.7. Methyl 2-(2-cyano-4-hydroxyphenyl)-2-methylopropionate (7d). *Procedure B*. Yield 76 mg, 69%, pale yellow crystals mp 134–135°C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): 7.28 (d, 1H, *J*=8.3 Hz), 7.01 (d, 1H, *J*=2.6 Hz), 6.96 (dd, 1H, *J*=8.3, 2.6 Hz), 3.81 (s, 3H), 1.66 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 178.1, 154.8, 139.5, 127.3, 121.1, 120.3, 117.8, 111.9, 52.9, 46.8, 26.8. EIMS(+) 219 (9.4), 203 (2.9), 193 (1.7), 187 (6.4), 160 (100.0), 144 (11.0), 132 (29.1). HR EIMS calcd for $C_{12}H_{13}NO_3$ M=219.08954. Found: 219.08807.

4.2.8. Ethyl (5-chloro-2-nitrophenyl)acetate (8a). *Procedure A*. Yield 16 mg, 13%, yellow crystals mp 59–60°C (EtOH), (lit.[16]61–63°C). ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (d, 1H, *J*=8.7 Hz), 7.45 (dd, 1H, *J*=8.7, 2.3 Hz), 7.35 (d, 1H, *J*=2.3 Hz), 4.22 − 4.11 (m, 2H), 4.00 (s, 2H), 1.26 (dt, 3H, *J*=7.1, 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 172.3, 169.3, 139.8, 133.2, 131.8, 128.7, 126.8, 61.5, 39.7, 14.1.

4.2.9. Ethyl (5-chloro-2-hydroxyphenyl)acetate (8b). *Procedure B*. Yield 67 mg, 62%, colorless crystals mp 62–63°C (EtOH), (lit.[17] 47°C). ^{1}H NMR (400 MHz, $CDCl_3$): 7.68 (s broad, 1H), 7.14 (dd, 1H, *J*=8.7, 2.5 Hz), 7.08 (d, 1H, *J*=2.5 Hz), 6.86 (d, 1H, *J*=8.7 Hz), 4.21 (q, 2H, *J*=7.1 Hz), 3.63 (s, 2H), 1.30 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 173.6, 153.9, 130.5, 128.9, 125.3, 122.2, 118.9, 62.2, 37.7, 14.0. Anal. calcd for $C_{10}H_{11}ClO_3$: C, 55.96; H, 5.17; Cl, 16.52. Found: C, 55.76; H, 5.25; Cl, 15.96.

4.2.10. 2-(2-Chloro-4-hydroxyphenyl)cycloheksanone (8c). *Procedure B*. Yield 31 mg, 21%, pale yellow crystals mp 131–132°C (Et_2O/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): 6.96 (d, 1H, *J*=8.5 Hz), 6.71 (d, 1H, *J*=2.5 Hz), 6.60 (dd, 1H, *J*=8.5, 2.5 Hz), 4.06–3.96 (m, 1H), 2.60–2.53 (m, 2H), 2.29–2.14 (m, 2H), 2.08–1.94 (m, 2H), 1.92–1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 212.2, 155.7, 134.1, 129.5, 127.5, 116.6, 114.5, 53.5, 42.3, 33.8, 27.7, 25.6. Anal. calcd for $C_{12}H_{13}O_2Cl$: C, 64.15; H, 5.83; Cl, 15.78. Found: C, 64.01; H, 6.09; Cl, 15.56.

4.3. Oxidation of silylated σ^H adducts of carbanion of 2-phenylpropionitrile to nitrobenzene with DMD

To a stirred solution of *t*-BuOK (123 mg, 1.1 mmol) in THF (5 mL) cooled to −70°C, under argon a solution of 2-phenylpropionitrile (144 mg, 1.1 mmol) and nitrobenzene (123 mg, 1 mmol) in THF (1 mL) was added dropwise during 1 min. After that the mixture was stirred for 5 min and Me_3SiCl (120 mg, 1.1 mmol) in THF (1 mL) was added. The mixture was stirred for 5 min water (18 μL, 1 mmol) and after 2 min an acetone solution of DMD (ca. 1.1 mmol, 19 mL of ca. 0.06 M) was added. After 5 min of further stirring, saturated aqueous NH_4Cl (0.1 mL) was added and the cooling bath was removed. The solution was dried over anhydrous $MgSO_4$. The solid phase was removed by filtration and washed with acetone (40 mL). The solvents were evaporated (25°C, 15 Torr). The products were purifed by column chromatography on silica gel with mixture hexane/ethyl acetate 20:1 as an eluent to give **1** (197 mg, 78%) and nitrobenzene (16 mg, 13%).

4.3.1. 2-Phenyl-2-(4-nitrophenyl)propionitrile (1). Yellow crystals mp 79–81°C (EtOH), (lit.[1] 76°C). Spectroscopic data consistent with that reported in the literature.[1]

The same reaction without Me_3SiCl gave **2** (181 mg, 81%) and **1** (18 mg, 7%).[2]

4.3.2. 2-Phenyl-2-(4-hydroxyphenyl)propionitrile (2). Colorless crystals mp 84–86°C (hexane/CH_2Cl_2), (lit.[2] 84–86°C). Spectroscopic data consistent with that reported in the literature.[2]

4.4. Oxidative substitution of hydrogen in nitrobenzene with lithium and tetraalkyl ammonium enolates of methyl isobutyrate

To a stirred solution of LDA (1.5 mmol, 0.8 mL, 1.8 M) in THF (10 mL) cooled to −70°C, under argon, methyl isobutyrate (154 mg, 1.5 mmol) was added. The solution was stirred for 10 min and

(a) Treated with $Bu_4N^+Br^-$, $Et_3(PhCH_2)N^+Cl^-$, $Bu_4N^+BF_4^-$ (3 mmol), stirred for 15 min and nitrobenzene (123 mg, 1 mmol) was added.
(b) Stirred additional 15 min and nitrobenzene (123 mg, 1 mmol) was added.

After 10 min powdered $KMnO_4$ (160 mg, 1 mmol) and liquid ammonia (ca. 10 mL, −70°C) was added to these mixtures, and after 15 min., NH_4Cl (212 mg, 4 mmol) was added. The cooling bath was removed and ammonia was evaporated. A saturated solution of oxalic acid in aq. HCl

(20 mL, 10%) was added to the residue and the mixture was extracted with CH_2Cl_2 (4×10 mL). The combined organic layers were dried over $MgSO_4$, filtered through silica gel and the solvent was evaporated (25°C, 15 Torr).

The product **6a** was purified by column chromatography on silica gel with hexane/ethyl acetate 20:1 as an eluent, yields of **6a** are given in Table 1.

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