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Nucleophilic aromatic substitution reaction of nitroarenes with alkyl- or arylthio groups in dimethyl sulfoxide by means of cesium carbonate

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Abstract—Treatment of nitroarenes having electron-withdrawing groups at the *ortho* or *para* position with alkanethiol in the presence of cesium carbonate in dimethyl sulfoxide at 25 °C leads to nucleophilic displacement of the nitro group with the alkylthio group. Cesium carbonate is superior to other bases such as potassium carbonate, sodium carbonate, and triethylamine. The cesium-mediated nucleophilic aromatic substitution reaction provides a mild yet powerful and user-friendly protocol for the synthesis of aryl sulfides.

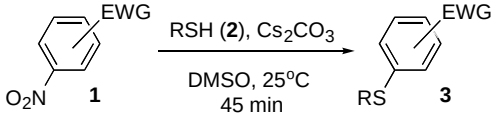
1. Introduction

Nucleophilic aromatic substitution reactions (S_NAr reactions) of nitroarenes that have strong electron-withdrawing groups at the *ortho* or *para* positions are well-known processes.[1] Here, we report an improved method for S_NAr reactions of activated nitroarenes with thiols. We have been interested in the excellent nucleophilicity of thiols in combination with cesium base,[2] since the development of truly powerful and highly reliable bond-forming reactions have attracted increasing attention.[3,4] The present cesium-mediated reaction is high-yielding and rapid, compared with similar reactions mediated by other bases,[1,5] and will be an extremely useful tool for conjugation chemistry through the formation of an sp^2-carbon–sulfur covalent bond.

2. Results and discussions

The reaction of 4-nitrobenzaldehyde (**1a**) with odorless 1-dodecanethiol (**2a**)[6] was chosen as a model reaction. Treatment of **1a** (0.50 mmol) with **2a** (0.60 mmol) in dimethyl sulfoxide (DMSO, 3 mL) in the presence of cesium carbonate (0.60 mmol) at 25 °C for 45 min provided the corresponding sulfide **3a** in 97% yield (Table 1, entry 1). Cesium carbonate[7] proved to be most powerful among bases we tested. Use of potassium carbonate and sodium carbonate resulted in lower yields, 46 and 11%, respectively. Organic bases such as triethylamine were far less effective. In the previous report,[1b] the success of the displacement is crucially due to the use of

Table 1. Cesium-mediated S_NAr reactions of nitroarenes with thiols



Entry	EWG	R	Yield (%)
1	4-CHO (**1a**)	$^nC_{12}H_{25}$ (**2a**)	97 (**3a**)
2	2-CHO (**1b**)	$^nC_{12}H_{25}$ (**2a**)	98 (**3b**)
3	4-NO_2 (**1c**)	$^nC_{12}H_{25}$ (**2a**)	88 (**3c**)
4	4-$COCH_3$ (**1d**)	$^nC_{12}H_{25}$ (**2a**)	88 (**3d**)
5	4-$COOCH_3$ (**1e**)	$^nC_{12}H_{25}$ (**2a**)	93 (**3e**)
6	4-CN (**1f**)	$^nC_{12}H_{25}$ (**2a**)	87 (**3f**)
7	4-F (**1g**)	$^nC_{12}H_{25}$ (**2a**)	—[a]
8	4-CHO (**1a**)	Ph (**2b**)	91 (**3g**)
9	4-CHO (**1a**)	CH_2=$CHCH_2$ (**2c**)	69 (**3h**)
10	4-CHO (**1a**)	PhCH=$CHCH_2$ (**2d**)	84 (**3i**)
11	4-CHO (**1a**)	$^tC_4H_9$ (**2e**)	89 (**3j**)
12	4-CHO (**1a**)	$HOCH_2CH_2$ (**2f**)	99 (**3k**)
13	H	$^nC_{12}H_{25}$ (**2a**)	<1 (**3l**)[b]

[a] 4-(Dodecylthio)nitrobenzene was obtained in 100% yield.
[b] The reaction was performed at 90 °C for 4 h.

Keywords: Cesium; Thiol; Sulfide; Nitroarene; Nucleophilic aromatic substitution reaction.
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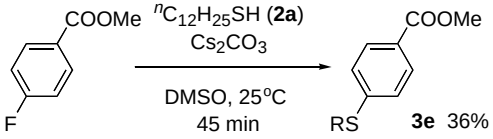
hexamethylphosphoramide (HMPA) and the use of DMSO resulted in lower efficiency. We chose DMSO as a solvent to avoid using carcinogenic HMPA.[8] Fortunately, the cesium-mediated displacement went to completion within 45 min at 25 °C. While 0.50 equiv of cesium carbonate effected the S_NAr reaction to yield **3a** in 87% yield, a stoichiometric amount of cesium carbonate is essential to attain quantitative reactions. Catalytic amounts of cesium carbonate resulted in poor conversions even with prolonged reaction time (20 mol%, 36%; 10 mol%, 17%; 5 mol%, 4% after 24 h).

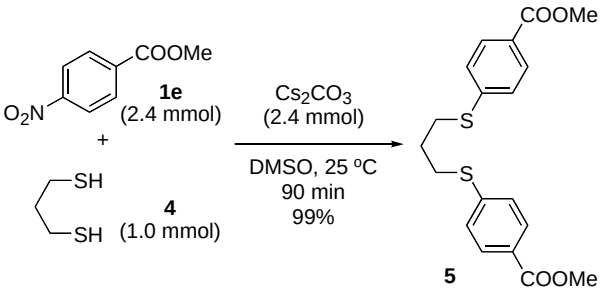
The reaction of 2-nitrobenzaldehyde (**1b**) proceeded almost quantitatively (entry 2). Not only a formyl group but also other electron-withdrawing groups such as acetyl and cyano groups enhanced the displacement reaction (entries 3–6). It is worth noting that the S_NAr reaction of methyl ester **1e** predominated over possible cleavage of the methyl ester linkage.[9] Fluoronitrobenzene **1g** underwent an S_NAr reaction at the fluorinated carbon to furnish 4-(dodecylthio)-nitrobenzene (entry 7). Nitrobenzene itself and 3-nitrobenzaldehyde resisted the S_NAr sulfidation under the same conditions. Aromatic thiol **2b**, allylic thiols **2c** and **2d**, and sterically demanding **2e** underwent the S_NAr displacement smoothly (entries 8–11). The hydroxy group of **2f** did not retard the reaction (entry 12). An additional electron-withdrawing group on nitrobenzene is essential. The reaction of nitrobenzene with **2a** failed to afford the corresponding product even at an elevated temperature (entry 13).

Nitroarenes are the better substrates for the S_NAr sulfidation reaction than the corresponding fluoroarenes that are recognized to be the standard substrates.[10] For instance, the reaction of methyl 4-fluorobenzoate with **2a** for 45 min provided **3e** in only 36% yield, leaving 60% of methyl 4-fluorobenzoate untouched (Eq. 1). It is worth noting that the chromatographic separation of **3e** and the starting fluoroarene on silica gel was quite difficult due to their comparable R_f values. The S_NAr sulfidation reaction with nitroarenes is thus advantageous with regard to facile purification procedure when needed as well as the superb efficiency.

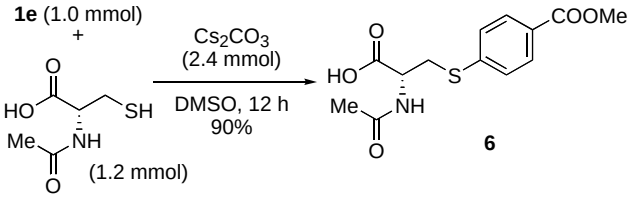


(1)

The reaction was efficient enough to allow multiple carbon–sulfur bond formations in one pot. Dithiol **4** underwent the S_NAr reactions with 2.4 equiv of nitro ester **1e** and cesium carbonate to provide **5** quantitatively (Eq. 2). Selective arylation at sulfur was also observed in the reaction of *N*-acetyl-L-cysteine, albeit a longer reaction time was necessary (Eq. 3). The longer reaction time would be due to the carboxy group. No observable racemization took place. The perfect reactivity of the sulfur moieties demonstrates that the present carbon–sulfur bond formation reaction is applicable to conjugation chemistry.



(2)



(3)

3. Summary

We have disclosed extremely powerful conditions for S_NAr reactions of activated nitroarenes with thiols. Cesium carbonate serves quite effectively in DMSO, which will allow us to use an sp^2-carbon–sulfur bond formation as a useful tool for conjugation chemistry.

4. Experimental

4.1. Cesium-mediated S_NAr reaction of nitroarenes with thiols

The reaction of dodecanethiol with 4-nitrobenzaldehyde is representative (Table 1, entry 1). Cesium carbonate (0.20 g, 0.60 mmol) was placed in a 20-mL reaction flask under argon. Dimethyl sulfoxide (3.0 mL), 4-nitrobenzaldehyde (**1a**, 0.076 g, 0.50 mmol), and dodecanethiol (**2a**, 0.12 g, 0.60 mmol) were added at 25 °C. The mixture was stirred for 45 min. Water (10 mL) was added, and the product was extracted with hexane–ethyl acetate (10/1, 10 mL×3). The combined organic layer was dried over sodium sulfate. Concentration followed by purification on silica gel afforded 4-dodecylthiobenzaldehyde (**3a**, 0.15 g, 0.49 mmol, 97%) as a yellow solid.

4.2. Characterization data

4.2.1. 4-Dodecylthiobenzaldehyde (3a). IR (Nujol) 2924, 2853, 2731, 2345, 1701, 1591, 1560, 1466, 1383, 1261, 1213, 1169, 1090, 1049, 837, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=7.0 Hz, 3H), 1.09–1.37 (m, 16H), 1.46 (tt, J=7.0, 7.5 Hz, 2H), 1.71 (tt, J=7.0, 7.5 Hz, 2H), 3.00 (t, J=7.5 Hz, 2H), 7.35 (d, J=8.5 Hz, 2H), 7.76 (d, J=8.5 Hz, 2H), 9.92 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.09, 22.66, 28.62, 28.88, 29.12, 29.32, 29.45, 29.54, 29.60, 29.61, 31.80, 31.89, 126.27, 129.98, 133.08, 147.15, 191.19. Found: C, 74.22; H, 10.05%. Calcd for $C_{19}H_{30}OS$: C, 74.45; H, 9.86%. Mp 33.3–34.0 °C.

4.2.2. 2-Dodecylthiobenzaldehyde (3b). IR (neat) 2924, 2853, 2731, 1695, 1587, 1560, 1460, 1439, 1396, 1261, 1196, 1128, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=7.0 Hz, 3H), 1.21–1.35 (m, 16H), 1.45 (tt, J=7.5, 7.5 Hz, 2H), 1.70 (tt, J=7.5, 7.5 Hz, 2H), 2.95 (t, J=7.5 Hz, 2H), 7.30 (dd, J=7.0, 7.5 Hz, 1H), 7.42 (d, J=8.0 Hz, 1H), 7.51 (dd, J=7.0, 8.0 Hz, 1H), 7.84 (d, J=7.5 Hz, 1H), 10.39 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.09, 22.64, 28.48, 28.93, 29.12, 29.30, 29.43, 29.53, 29.57, 29.59, 31.86, 33.18, 125.09, 127.97, 131.98, 133.82, 133.83, 142.30, 191.50. Found: C, 74.55; H, 9.95%. Calcd for $C_{19}H_{30}OS$: C, 74.45; H, 9.86%.

4.2.3. 1-Dodecylthio-4-nitrobenzene (3c). IR (Nujol) 2224, 2853, 2332, 2235, 1578, 1508, 1466, 1337, 1082, 962, 851, 837, 745, 723, 669, 617 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=7.0 Hz, 3H), 1.20–1.38 (m, 16H), 1.46 (tt, J=7.5, 7.5 Hz, 2H), 1.72 (tt, J=7.5, 7.5 Hz, 2H), 3.01 (t, J=7.5 Hz, 2H), 7.31 (d, J=9.5 Hz, 2H), 8.12 (d, J=9.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.11, 22.67, 28.44, 28.86, 29.09, 29.32, 29.44, 29.53, 29.60, 29.61, 31.89, 31.90, 123.91, 125.93, 144.79, 148.17. Found: C, 66.68; H, 8.96%. Calcd for $C_{18}H_{29}NO_2S$: C, 66.83; H, 9.04%. Mp 49.5–50.5 °C.

4.2.4. 4-Dodecylthioacetophenone (3d). IR (Nujol) 2920, 2851, 2345, 1678, 1591, 1462, 1377, 1364, 1053, 976, 816, 719, 590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=7.0 Hz, 3H), 1.20–1.36 (m, 16H), 1.45 (tt, J=7.5, 7.5 Hz, 2H), 1.70 (tt, J=7.5, 7.5 Hz, 2H), 2.57 (s, 3H), 2.99 (t, J=7.5 Hz, 2H), 7.30 (d, J=9.0 Hz, 2H), 7.86 (d, J=9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.12, 22.68, 26.44, 28.70, 28.89, 29.13, 29.33, 29.46, 29.55, 29.61, 29.62, 31.89, 31.90, 126.16, 128.72, 133.63, 145.01, 197.21. Found: C, 74.76; H, 9.87%. Calcd for $C_{20}H_{32}OS$: C, 74.94; H, 10.06%. Mp 69.5–70.2 °C.

4.2.5. Methyl 4-dodecylthiobenzoate (3e). IR (Nujol) 2918, 2851, 1724, 1678, 1599, 1462, 1398, 1366, 1290, 1196, 1115, 1092, 831, 816, 754, 719, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=7.0 Hz, 3H), 1.20–1.35 (m, 16H), 1.44 (tt, J=7.0, 7.5 Hz, 2H), 1.69 (tt, J=7.0, 7.5 Hz, 2H), 2.98 (t, J=7.5 Hz, 2H), 3.90 (s, 3H), 7.28 (d, J=8.5 Hz, 2H), 7.92 (d, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.12, 22.68, 28.70, 28.88, 29.13, 29.33, 29.46, 29.55, 29.61, 29.62, 31.90, 31.99, 52.02, 126.18, 126.43, 129.86, 144.51, 166.85. Found: C, 71.27; H, 9.41%. Calcd for $C_{20}H_{32}O_2S$: C, 71.38; H, 9.58%. Mp 64.5–65.2 °C.

4.2.6. 4-Dodecylthiobenzonitrile (3f). IR (Nujol) 2918, 2851, 2230, 1919, 1593, 1547, 1487, 1470, 1431, 1402, 1379, 1346, 1302, 1244, 1182, 1126, 1089, 1070, 1015, 824, 779, 762, 719, 592, 544 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=7.0 Hz, 3H), 1.21–1.36 (m, 16H), 1.44 (tt, J=7.0, 7.5 Hz, 2H), 1.69 (t, J=7.5, 7.5 Hz, 2H), 2.97 (t, J=7.5 Hz, 2H), 7.29 (d, J=8.5 Hz, 2H), 7.52 (d, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.11, 22.67, 28.51, 28.84, 29.09, 29.32, 29.44, 29.53, 29.59, 29.61, 31.82, 31.88, 107.80, 118.98, 126.57, 132.16, 145.31. Found: C, 75.12; H, 9.50%. Calcd for $C_{19}H_{29}NS$: C, 75.19; H, 9.63%. Mp 50.0–50.5 °C.

4.2.7. 4-Phenylthiobenzaldehyde (3g). IR (neat) 3059, 2831, 2735, 1699, 1670, 1593, 1562, 1475, 1441, 1387, 1358, 1302, 1285, 1211, 1169, 1078, 1024, 1013, 1001, 920, 837, 816, 750, 692, 507, 478 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.24 (d, J=8.0 Hz, 2H), 7.41–7.46 (m, 3H), 7.51–7.56 (m, 2H), 7.72 (d, J=8.0 Hz, 2H), 9.91 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 127.10, 129.14, 129.77, 130.09, 131.16, 133.59, 134.34, 147.23, 191.18. Found: C, 72.64; H, 4.83%. Calcd for $C_{13}H_{10}OS$: C, 72.87; H, 4.70%.

4.2.8. 4-(2-Propenylthio)benzaldehyde (3h). IR (neat) 2922, 2833, 2736, 1697, 1672, 1637, 1591, 1562, 1489, 1410, 1387, 1306, 1285, 1215, 1171, 1090, 989, 926, 837, 812, 739, 696, 536, 486 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.68 (d, J=6.5 Hz, 2H), 5.19 (d, J=9.0 Hz, 1H), 5.31 (d, J=15.5 Hz, 1H), 5.91 (ddd, J=6.5, 9.0, 15.5 Hz, 1H), 7.38 (d, J=6.5 Hz, 2H), 7.77 (d, J=6.5 Hz, 2H), 9.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 35.02, 118.68, 126.90, 129.91, 132.28, 133.34, 145.82, 191.24. Found: C, 67.26; H, 5.67%. Calcd for $C_{10}H_{10}OS$: C, 67.38; H, 5.65%.

4.2.9. 4-[(*E*)-3-Phenyl-2-propenylthio]benzaldehyde (3i). IR (Nujol) 2924, 2855, 2731, 1696, 1589, 1560, 1460, 1377, 1084, 1028, 966, 837, 814, 762, 745, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.85 (d, J=7.0 Hz, 2H), 6.26 (dt, J=16.0, 7.0 Hz, 1H), 6.62 (d, J=16.0 Hz, 1H), 7.22–7.37 (m, 5H), 7.42 (d, J=8.0 Hz, 2H), 7.77 (d, J=8.0 Hz, 2H), 9.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 34.95, 123.56, 126.38, 127.16, 127.90, 128.60, 130.01, 133.47, 133.73, 136.25, 145.81, 191.27. Found: C, 75.29; H, 5.53%. Calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55%. mp 91.0–92.5 °C.

4.2.10. 4-(1,1-Dimethylethylthio)benzaldehyde (3j). IR (neat) 2963, 2924, 2899, 2862, 2831, 2729, 1705, 1593, 1562, 1474, 1458, 1366, 1298, 1281, 1205, 1167, 1086, 1016, 826, 718, 698, 503 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (s, 9H), 7.69 (d, J=8.0 Hz, 2H), 7.83 (d, J=8.0 Hz, 2H), 10.04 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 31.05, 47.10, 129.37, 135.77, 136.97, 141.20, 191.66. Found: C, 68.28; H, 7.31%. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26%.

4.2.11. Methyl 4-(2-hydroxyethylthio)benzoate (3k). IR (Nujol) 3344, 2924, 2855, 1720, 1597, 1460, 1377, 1281, 1115, 1057, 1013, 959, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.11 (s, 1H), 3.20 (t, J=6.5 Hz, 2H), 3.82 (t, J=6.5 Hz, 2H), 3.89 (s, 3H), 7.34 (d, J=9.0 Hz, 2H), 7.92 (d, J=9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 35.37, 52.10, 60.40, 127.20, 127.30, 130.01, 142.40, 166.67. Found: C, 56.44; H, 5.67%. Calcd for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70%. Mp 58.0–59.5 °C.

4.2.12. 1,3-Di(4-methoxycarbonylphenylthio)propane (5). IR (Nujol) 2924, 2853, 1722, 1595, 1435, 1377, 1277, 1250, 1192, 1113, 1015, 961, 847, 829, 756, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.06 (quint, J=7.0 Hz, 2H), 3.14 (t, J=7.0 Hz, 4H), 3.90 (s, 6H), 7.29 (d, J=9.0 Hz, 4H), 7.91 (d, J=9.0 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 27.89, 31.05, 52.34, 127.02, 127.32, 130.26, 143.30, 166.94. Found: C, 60.36; H, 5.38%. Calcd for $C_{19}H_{20}O_4S_2$: C, 60.61; H, 5.35%. Mp 98.5–100.0 °C.

4.2.13. *N*-Acetyl-*S*-(4-methoxycarbonylphenyl)-L-cysteine (6). IR (Nujol) 3337, 2924, 2855, 2532, 2104, 1715, 1618, 1597, 1560, 1491, 1458, 1439, 1377, 1277, 1232, 1186, 1109, 1013, 758 cm^{-1}; ^1H NMR (CD_3OD) δ 1.90 (s, 3H), 3.26–3.36 (m, 1H), 3.54–3.64 (m, 1H), 3.88 (s, 3H), 4.60–4.66 (m, 1H), 7.43 (d, J=8.7 Hz, 2H), 7.91 (d, J=8.7 Hz, 2H); ^{13}C NMR (CD_3OD) δ 22.35, 34.84, 52.60, 53.37, 128.40, 128.48, 130.81, 144.11, 167.88, 172.82, 173.05. Found: C, 52.37; H,

5.08%. Calcd for $C_{13}H_{15}NO_5S$: C, 52.52; H, 5.08%. Mp 158.5–159.5 °C. Retention time: 7.5 min (CHIRALCEL® OJ-H column, 4.6×250 mm, Daicel Chemical Industries, hexane/2-propanol = 80:20, 1.3 mL/min, 40 °C, 254 nm UV detector, retention time of minor isomer: 9.2 min).

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