

Molybdenum-mediated imido-transfer reaction of *N*-sulfinylamines with dimethylformamide

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Characteristics for compounds 2b–d, 3b–d.

N,N-dimethyl-*N'*-(*o*-trifluorophenyl)formamidine **2b**. Orange oil. Yield 0.47 g (73%), bp 78–82 °C (0.2 Torr). IR (ν/cm^{-1}): 1640 (C=N). ^1H NMR, δ : 7.55 (d, J 7.27 Hz, H_{Ar} , 1H), 7.43 (s, CH, 1H), 7.37 (t, J 7.67 Hz, H_{Ar} , 1H), 7.01 (t, J 7.57 Hz, H_{Ar} , 1H), 6.87 (d, J 7.87 Hz, H_{Ar} , 1H), 3.02 (s, $\text{N}(\text{CH}_3)_2$, 6H). ^{19}F NMR, δ : 16.88 (s, CF_3). MS, m/z (%): 216 $[\text{M}]^+$ (30), 201 (8), 177 (25), 154 (24), 147 (100), 145 (37), 75 (8). Calc. for $\text{C}_{10}\text{H}_{11}\text{F}_3\text{N}_2$ (%): C, 55.55; H, 5.13; N, 12.96. Found (%): C, 55.37; H, 5.11; N, 12.90.

N,N-dimethyl-*N'*-(*o*-fluorophenyl)formamidine **2c**. The spectroscopically estimated yields are 44% for formamidine **2c** and 43% for sulfurdiimine **3c**. The product **2c** was identified on the basis of spectral data. IR (ν/cm^{-1}): 1640 (C=N). ^1H NMR, δ : 7.55 (s, CH, 1H), 7.03–6.88 (m, H_{Ar} , 4H) 3.00 (br. s, $\text{N}(\text{CH}_3)_2$, 6H). ^{19}F NMR, δ : -51.37 (s, F_{Ar}). MS, m/z (%): 166 $[\text{M}]^+$ (86), 151 (55), 147 (78), 124 (100), 122 (45), 109 (17), 103 (14), 95 (48), 91 (50), 75 (48).

N,N-dimethyl-*N'*-(*o*-methoxyphenyl)formamidine **2d**. The spectroscopically estimated yields are 53% for formamidine **2d** and 25% for sulfurdiimine **3d**. The product **2d** was identified by comparison of its spectral data with the reported ones.¹ IR (ν/cm^{-1}): 1636 (C=N). ^1H NMR, δ : 7.50 (s, CH, 1H), 7.00–6.94 (m, H_{Ar} , 1H), 6.88–6.77 (m, H_{Ar} , 3H), 3.83 (s, OCH_3 , 3H), 3.02 (br. s, $\text{N}(\text{CH}_3)_2$, 6H). MS, m/z (%): 178 $[\text{M}]^+$ (40), 163 (10), 147 (100), 135 (26), 134 (19), 133 (24), 120 (22), 106 (27), 94 (9), 91 (9), 77 (15).

Di-(*o*-trifluoromethylphenyl)sulfodiimine **3b**. Yield 0.27 g (52 %), bp 98–103°C (0.1 Torr). ^1H

NMR, δ : 7.60 (d, J 7.53 Hz, 2H), 7.21 – 7.11 (m, 6H). ^{19}F NMR, δ : 15.91 (s, CF_3). MS, m/z (%): 350 $[\text{M}]^+$ (17), 331 (4), 281 (100), 191 (8), 177 (16), 172 (4), 145 (16), 126 (6), 122 (4). Calc. for $\text{C}_{14}\text{H}_8\text{F}_6\text{N}_2\text{S}$ (%): C, 48.00; H, 2.30. Found (%): C, 47.97; H, 2.48.

Di-(o-fluorophenyl)sulfurdiimine 3c. Spectroscopically estimated yield is 35 %. Product **3c** was identified on the basis of spectral data. ^1H NMR, δ : 7.25 – 7.19 (m, 2H), 7.01 – 6.93 (m, 4H), 6.83 – 6.76 (m, 2H). ^{19}F NMR, δ : - 40.75 (c, F_{Ar}). MS, m/z (%): 250 $[\text{M}]^+$ (48), 249 (100), 231 (48), 180 (19), 179 (11), 164 (9), 141 (9), 140 (10), 127 (22), 122 (12), 91 (31).

Di-(o-methoxyphenyl)sulfurdiimine 3d. Orange crystals. Yield 0.23 g (55 %). mp 83–85°C (lit.² 89°C). ^1H NMR, δ : 6.99 (d, H_{Ar} , J 7.76 Hz, 2H), 6.93 (t, H_{Ar} , 2H), 6.71 (t, H_{Ar} , 2H), 6.49 (d, H_{Ar} , J 8 Hz, 2H), 3.60 (s, OCH_3 , 6H). MS, m/z (%): 274 $[\text{M}]^+$ (1), 259 (8), 243 (100), 228 (22), 200 (4), 156 (5), 120 (4). Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ (%): C, 61.29; H, 5.14; N, 10.21. Found (%): C, 61.44; H, 4.98; N, 9.98.

References

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2. H.-H. Hornhold and J. Beck, *J. Prakt. Chem.*, 1969, **311**, 621.