SUPPORTING INFORMATION

(Z)-1-Aryl-1-haloalkenes as Intermediates in the Vilsmeier Haloformylation of Arylketones

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¹H and ¹³C NMR and HRMS data for the new compounds 10a-f and 10h.

NMR spectra were recorded on 200 MHz Varian Gemini 2000 or 500 MHz Bruker Avance 500 (NOESY/ROESY work) spectrometers. For NMR, a sample was quickly passed through a short alumina column eluting with CH₂Cl₂ and evaporated. Mass spectra were recorded on a JEOL JMS SX102 mass spectrometer. **10a-b** are viscous oils and **10c-f** are white solids. Compounds are stored under argon at -20 °C.

1-Chloro-1-(2,4-dimethoxyphenyl)ethene 10a

¹H NMR (CHCl₃) δ 3.82 (3H, s), 3.85 (3H, s), 5.62 (1H, d, *J* = 1.10 Hz), 5.66 (1H, d, *J* = 0.73 Hz), 6.47 (2H, m), 7.41 (1H, m)

¹³C NMR (CHCl₃) δ 56.1, 56.3, 99.5, 104.8, 116.9, 120.6, 131.8, 136.8, 158.6, 162.0

HRMS 198.0448 calculated for C₁₀H₁₁ClO₂; found 198.0456

1-Bromo-1-(2,4-dimethoxyphenyl)ethene 10b

¹H NMR (CDCl₃) δ 3.82 (3H, s), 3.85 (3H, s), 5.86 (1H, d, *J* = 1.47 Hz), 5.95 (1H, d, *J* = 1.47 Hz), 6.46 (2H, m), 7.32 (1H, m)

¹³C NMR (CHCl₃) δ 55.4, 55.7, 98.8, 104.2, 121.0, 121.8, 126.4, 131.6, 157.6, 161.4

HRMS 241.9942 calculated for C₁₀H₁₁BrO₂; found 241.9954

Z-1-Chloro-1-(2,4-dimethoxyphenyl)propene 10c

¹H NMR (CDCl₃) δ 1.91 (3H, d, *J* = 6.60 Hz), 3.81 (3H, s), 3.83 (3H, m), 5.95 (1H, q, *J* = 6.60 Hz), 6.45 (2H, m), 7.24 (1H, m)

¹³C NMR (CDCl₃) δ = 15.0, 55.4, 55.7, 98.9, 104.1, 121.7, 125.1, 129.8, 131.2, 157.8, 160.9

HRMS 212.0604 calculated for C₁₁H₁₃ClO₂; found 212.0594

Z-1-Bromo-1-(2,4-dimethoxyphenyl)propene 10d

¹H NMR (CDCl₃) δ 1.90 (3H, d, *J* = 6.59 Hz), 3.81 (3H, s), 3.83 (3H, s), 5.99 (1H, q, *J* = 6.60 Hz), 6.45 (2H, m), 7.18 (1H, m)

^{13}C NMR (CDCl_3) δ 17.8, 55.4, 55.7, 98.8, 104.1, 121.7, 123.3, 128.3, 131.6, 157.8, 161.0

HRMS 256.0099 calculated for $\text{C}_{11}\text{H}_{13}\text{BrO}_2$; found 256.0111

Z-1-Chloro-1-(4-dimethylaminophenyl)propene 10e

^1H NMR (CDCl_3) δ 1.91 (3H, d, $J = 6.96$ Hz), 2.95 (6H, s), 6.01 (1H, q, $J = 6.96$ Hz), 6.65 (2H, m), 7.43 (2H, m)

^{13}C NMR (CDCl_3) δ 15.0, 40.4, 111.8, 118.5, 126.6, 127.2, 134.1, 150.3

HRMS 195.0815 calculated for $\text{C}_{11}\text{H}_{14}\text{ClN}$; found 195.0827

Z-1-Bromo-1-(4-dimethylaminophenyl)propene 10f

^1H NMR (CDCl_3) δ 1.91 (3H, d, $J = 6.59$ Hz), 2.97 (6H, s), 6.10 (1H, q, $J = 6.60$ Hz), 6.65 (2H, m), 7.40 (2H, m)

HRMS 212.0604 calculated for $\text{C}_{11}\text{H}_{14}\text{BrN}$; found 212.0594

Compound **10f** is unstable and readily forms the acetylenic compound (4-dimethylaminophenyl)propyne:

^1H NMR (CDCl_3) δ 2.03 (3H, s), 2.94 (6H, s), 6.61 (2H, m), 7.27 (2H, m)

^{13}C NMR (CDCl_3) δ 5.1, 41.0, 80.9, 83.6, 111.8, 112.6, 133.1, 150.4

HRMS 159.1048 calculated for $\text{C}_{11}\text{H}_{13}\text{N}$; found 159.1055

1-Chloro-1-(2-dimethylaminophenyl)ethene 10h

^1H NMR (CDCl_3) δ 2.82 (6H, s), 5.58 (1H, d, $J=1.10$ Hz), 5.62 (1H, d, $J=0.73$ Hz), 6.91 (2H, m), 7.28 (2H, m)

^{13}C NMR (CDCl_3) δ 43.2, 98.2, 115.8, 117.6, 120.4, 129.8, 131.1, 135.0, 140.1

M (m/z) 181

Synthesis of compound 11e:

Synthesis of 3-chloro-3-(4-dimethylaminophenyl)-2-methylpropenal 11e:

To an ice cooled solution of DMF (1.07 mmol) and 0.3 ml of CH_2Cl_2 under Ar, POCl_3 (0.92 mmol) was added dropwise. The solution was stirred for 30 minutes at 0 °C. Z-1-Chloro-1-(4-dimethylaminophenyl)propene **10e** (0.31 mmol) in 0.7ml of CH_2Cl_2 was added dropwise after which the reaction mixture was refluxed for 3 hours. The reaction was quenched with sat. NaOAc, extracted with CH_2Cl_2 and washed with brine and water.

After filtration the solvent was evaporated. The product was purified by flash chromatography (CH₂Cl₂-EtOAc 9:1). Purification afforded inseparable isomeric mixture (1:6 *E/Z* ratio) of 3-chloro-3-(4-dimethylaminophenyl)propenal as a yellow solid in 61% yield.

Z-11e ¹H NMR (CDCl₃) δ 2.07 (3H, s), 3.03 (6H, s), 6.68 (2H, m), 7.31 (2H, m), 9.51 (1H, s)

E-11e ¹H NMR (CDCl₃) δ 1.96 (3H, s), 3.04 (6H, s), 6.68 (2H, m), 7.31 (2H, m), 10.37 (1H, s)

HRMS 223.0774 (calculated 223.0764)