

Hydrolysis of (*Z*)-2-alkoxy-3-arylpropenals as a short-cut to benzylglyoxals

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(*Z*)-2-Methoxy-3-(4-chlorophenyl)propenal **3a** prepared by the described method.¹ Clear oil (viscous) liquid bright yellow. Yield after purification by chromatography on silica gel, eluent CH₂Cl₂, 0.87 g (62%). IR, ν , cm⁻¹: 2945, 2849, 2735, 1688 (C=O), 1589 (C=C), 1489, 1453, 1360, 1152, 1091, 1037, 1013, 811, 764. ¹H NMR (CDCl₃) δ : 3.97 (s, 3H, CH₃), 6.45 (s, 1H, CH=), 7.36 (d, 2H, H³, H⁵, *J* 8.6 Hz), 7.73 (d, 2H, H², H⁶, *J* 8.6 Hz), 9.33 (s, 1H, CHO). ¹³C NMR (CDCl₃) δ : 58.73 (CH₃), 128.90 (C³, C⁵), 131.29 (C², C⁶), 131.71 (C¹), 131.86 (=CH), 135.65 (C⁴), 154.00 (=C-OMe), 188.89 (CHO). GC-MS, *m/z* (%): 196 (90) [M]⁺, 166 [M⁺-OCH₂], 161 (81) [M⁺-Cl], 152 (36), 125 (100), 112 (5), 103 (14), 89 (77), 75 (12), 63 (21), 51 (7), 39 (6), 29 (5) [CHO]. Found (%): C, 61.0; H, 4.84; Cl, 17.97. Calc. for C₁₀H₉ClO₂ (%): C, 61.07; H, 4.58; Cl, 18.01.

(*Z*)-2-Butoxy-3-(4-chlorophenyl)propenal **3b** prepared by the described method.¹ Clear oil (viscous) liquid dark yellow. Yield after purification by chromatography on silica gel, eluent CH₂Cl₂, 1.23 g (51%). IR, ν , cm⁻¹: 2960, 2933, 2873, 1719, 1688 (C=O), 1589 (C=C), 1489, 1423, 1400, 1308, 1276, 1173, 1091, 1014, 826, 761. ¹H NMR (CDCl₃) δ : 0.94 (t, 3H, CH₃, *J* 7.3 Hz), 1.44 (m, 2H, CH₂), 1.72 (m, 2H, CH₂), 4.22 (t, 3H, OCH₂, *J* 6.6 Hz), 6.45 (s, 1H, CH=), 7.36 (d, 2H, H³, H⁵, *J* 8.4 Hz), 7.76 (d, 2H, H², H⁶, *J* 8.4 Hz), 9.32 (s, 1H, CHO). ¹³C NMR (CDCl₃) δ : 13.89 (CH₃), 19.16 (CH₂), 32.15 (CH₂), 71.23 (OCH₂), 128.98 (C³, C⁵), 128.66 (=CH), 131.34 (C², C⁶), 131.99 (CH=), 132.12 (C¹), 135.63 (C⁴), 153.72 (=C-OCH₂), 189.37 (CHO). In the NOESY spectra observed cross peaks of proton =CH with an proton of aldehyde and ortho-ring protons. GC-MS, *m/z* (%): 238 (39) [M]⁺, 182 (87), 166 (36), 147 (100), 136 (4), 125 (67), 101 (10), 89 (36), 75 (7), 57 (20), 41 (28), 29 (24) [CHO]. Found (%): C, 65.75; H, 6.33; Cl, 15.02. Calc. for C₁₃H₁₅ClO₂ (%): C, 65.41; H, 6.29; Cl, 14.88.

(*Z*)-2-Methoxy-3-(4-nitrophenyl)propenal **3c** prepared by the described method.¹ Clear oil (viscous) liquid. Yield after purification by chromatography on silica gel, eluent CH₂Cl₂, 0.44 g

(64 %). IR, ν , cm^{-1} : 2918, 2849, 1691 (C=O), 1593 (C=C), 1515, 1456, 1344, 1152, 1105, 1031, 865, 691. ^1H NMR (CDCl_3) δ : 4.1 (s, 3H, CH_3), 6.5 (s, 1H, $\text{CH}=\text{}$), 7.94 (d, 2H, H^2 , H^6 , J 8.6 Hz), 8.24 (d, 2H, H^3 , H^5 , J 8.6 Hz), 9.33 (s, 1H, CHO). ^{13}C NMR (CDCl_3) δ : 59.02 (OCH_3), 123.68 (C^3 , C^5), 128.66 ($=\text{CH}$), 130.43 (C^2 , C^6), 139.45 (C^1), 147.5 (C^4), 155.23 ($=\text{C}-\text{OMe}$), 188.71 (CHO). GC-MS, m/z (%): 207 (100) $[M]^+$, 190 (75), 177 (51), 160 (55), 147 (15) $[M^+ - \text{OMe} - \text{CHO}]$, 130 (44), 118 (93), 103 (24), 89 (89), 77 (29), 63 (39), 51 (14), 39 (13). Found (%): C, 58.00; H, 4.39; Cl, 6.80. Calc. for $\text{C}_{10}\text{H}_9\text{NO}_4$ (%): C, 57.97; H, 4.35; N, 6.76.

(*Z*)-2-Butoxy-3-(4-nitrophenyl)propenal **3d** prepared by the described method.¹ Clear oil (viscous) liquid bright orange. Yield after purification by chromatography on silica gel, eluent CH_2Cl_2 , 0.58 g (35%). IR, ν , cm^{-1} : 2960, 2934, 2893, 1691 (C=O), 1594 (C=C), 1518, 1343, 1179, 1106, 1026, 864, 691. ^1H NMR (CDCl_3) δ : 0.95 (t, 3H, CH_3 , J 7.4 Hz), 1.45 (m, 2H, CH_2), 1.73 (m, 2H, CH_2), 4.34 (t, 3H, OCH_2 , J 6.6 Hz), 6.49 (s, 1H, $\text{CH}=\text{}$), 7.95 (d, 2H, H^2 , H^6 , J 8.8 Hz), 8.22 (d, 2H, H^3 , H^5 , J 8.8 Hz), 9.40 (s, 1H, CHO). ^{13}C NMR (CDCl_3) δ : 13.89 (CH_3), 19.13 (CH_2), 32.48 (CH_2), 71.60 (OCH_2), 123.86 (C^3 , C^5), 128.86 ($=\text{CH}$), 130.47 (C^2 , C^6), 139.86 (C^1), 147.63 (C^4), 155.11 ($=\text{C}-\text{OCH}_2$), 189.13 (CHO). GC-MS, m/z (%): 249 (30) $[M]^+$, 207 (4), 193 (100), 177 (22), 164 (53), 147 (33), 133 (7), 118 (17), 102 (7), 89 (26), 76 (8), 57 (43), 41 (44), 27 (6). Found (%): C, 62.41; H, 6.11; N, 5.37. Calc. for $\text{C}_{13}\text{H}_{15}\text{NO}_4$ (%): C, 62.65; H, 6.02; N, 5.62.

References

1. N. A. Keiko, L. G. Stepanova, E. A. Verochkina and L. I. Larina, *Arkivoc*, 2010, (ii), 49.