Electronic supplementary information

Selective Etherification of Glycerol Acetals with Dimethyl Carbonate in the Presence of K_2CO_3 Catalyst

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Contents

Synthesis of DBnC

Dibenzyl carbonate was prepared *via* transesterification reaction of DMC with benzyl alcohol, by a two-step procedure reported in the literature.[1] Accordingly, in the first step, a mixture of benzyl alcohol (30 g, 0.28 mol), DMC (100 g, 1.11 mol) and hydrotalcite KW2000 (30 g) was set to react at 90 °C, for 24 hours. This allowed to isolate crude benzyl methyl carbonate (BMC) as a colourless oil in a 90% yield (42 g). In the second step, a mixture of BMC (42 g), benzyl alcohol (60 g, 56 mol), and hydrotalcite KW2000 (30 g) was set to react at 110 °C for 4 hours. Dibenzyl carbonate was purified by distillation under vacuum (130 °C, 0.7 mmHg): yield was 56 g (83 %, colorless solid). Spectroscopic properties were in agreement with those reported in the literature.[2]

GC calibration curves

The mass balance of the methylation of GlyF with DMC. GC calibration curves for GlyF and O-methyl derivatives **2a-2b** were obtained using *n*-dodecane (C_{12}) as internal standard. As an example, in the case of GlyF, four different solutions of the commercial mixture of **1a-1b** isomers in DMC were prepared at 0.38 M, 0.15 M, 0.075 M and 0.03 M concentration, respectively. In particular, 0.078, 0.195, 0.390 and 0.989 g of **1a-1b** were used. To each solution, the same quantity of *n*-dodecane (0.95 mmol) was added. Figure 1 shows the results of the calibration test.

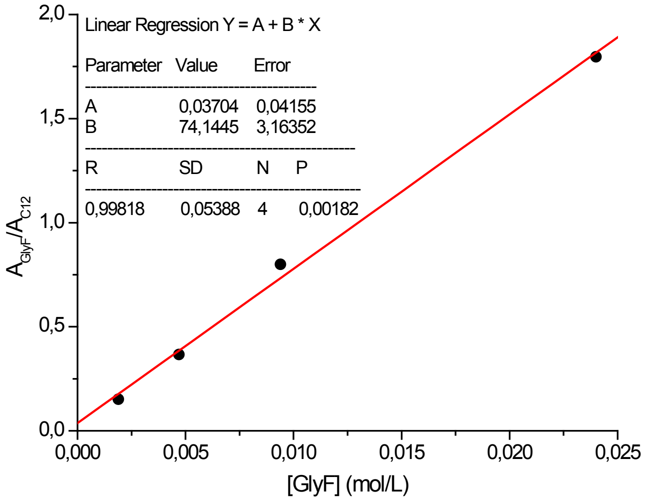


Figure 1. Calibration curve for GlyF. *n*-Dodecane (C12) was the internal standard. A_{GlyF}/A_{C12} was the ratio of GC area responses of GlyF and C_{12}.

In the case of compounds **3a-3b**, the corresponding calibration curve was not obtained. However, the GC response of three solutions containing equimolar quantities of GlyF and (**3a-3b**) in diethyl ether, was compared. In particular 0.050, 0.25, 1.25 g of GlyF, and 0.078, 0.39, 1.95 g of **3a-3b** were used to obtained 10 mL of 0.0048, 0.024 and 0.12 M solutions. In this range of molarity, the difference in the GC area responses between GlyF and (**3a-3b**) varied from 6 to 12%. However, compounds (**3a-3b**) were present in very low amounts (≤ 5%) at the end of reactions of GlyF with DMC, determining a very modest inaccuracy in the mass balance of final reaction mixtures.

The mass balance of the methylation of Solketal with DMC. The same procedure described to obtain the calibration curve for GlyF was used for Solketal and its O-methyl derivative **2c**. As an example, four different solutions of Solketal in DMC were prepared at 0.38 M, 0.15 M, 0.075 M and 0.03 M concentration, respectively. In particular, 0.99, 0.248, 0.496 and 1.256 g of **1c** were used. To each solution, the same quantity of *n*-dodecane (0.95 mmol) was added. The plot of the ratio of GC area responses of Solketal and C_{12} ($A_{\mathbf{1c}}/A_{C12}$) *vs* the Solketal concentration allowed to obtain an excellent linear relationship with a correlation coefficient (R) of 0.9993.

MS spectra of compounds 6c and 7c

4-(ethoxymethyl)-2,2-dimethyl-1,3-dioxolane (6c). GC/MS (relative intensity, 70 eV) m/z: 160 (M^+, <1%), 115 ($[M-OCH_2CH_3]^+$, 100), 101 ($[M-H_2COCH_2CH_3]^+$, 40), 73 (22), 72 (28), 59 (61), 57 (86).

Ethyl(2,2-dimethyl-1,3-dioxolan-4-yl)methylcarbonate (7c). GC/MS (relative intensity, 70 eV) m/z: 204 (M^+, <1%), 189 ($[M-CH_3]^+$, 64), 161 (61), 101 ($[M-H_2COCO_2CH_2CH_3]^+$, 70), 73 (29), 72 (40), 61 (37), 59 (64), 57 (100).

MS Spectra of C5 and C6 isomers of compounds 2a-2b and 3a-3b.

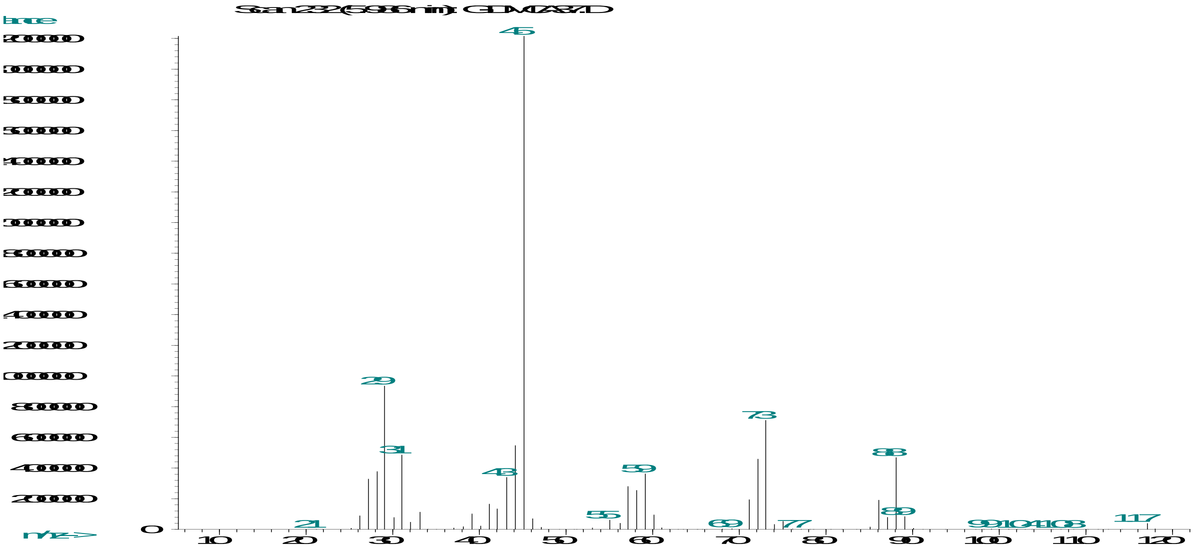


Figure 2. MS spectra of **2a** product.

GC/MS (relative intensity, 70 eV) m/z: 118 (M^+, <1%), 117 ($[M-H]^+$, 1), 88 $[M-H_2CO]^+$, 15), 73 ($[M-H_2COCH_3]^+$, 22), 72 (14), 59 (11), 45 ($[CH_2=OCH_3]^+$, 100), 44 (17), 43 (11), 31 (15), 29 (29), 28 (12), 27 (10).

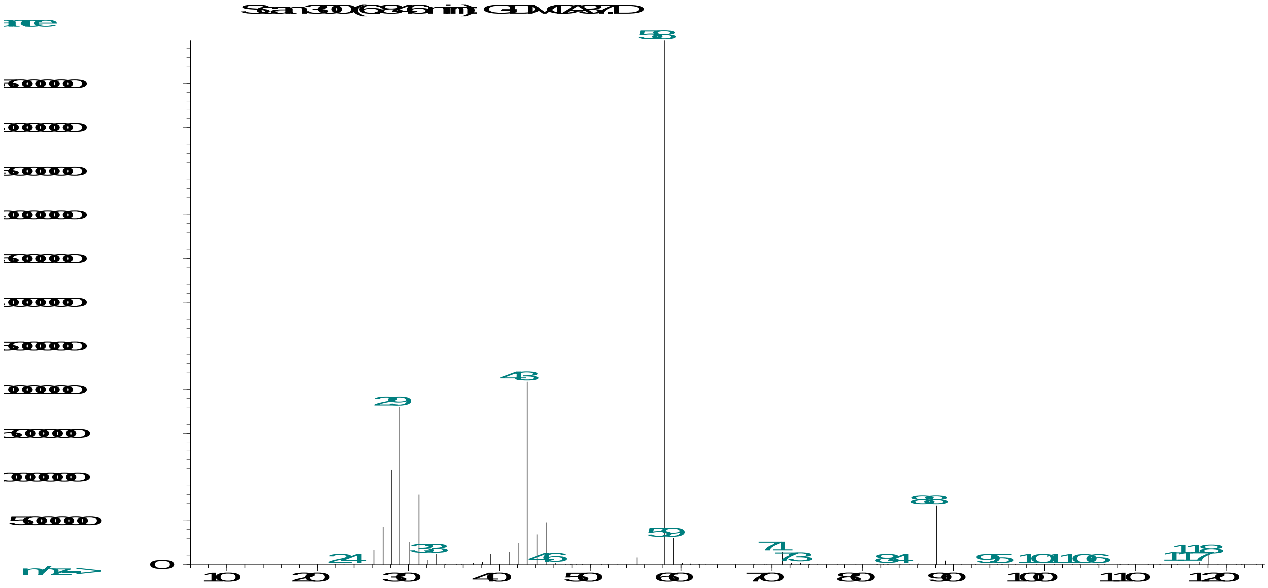
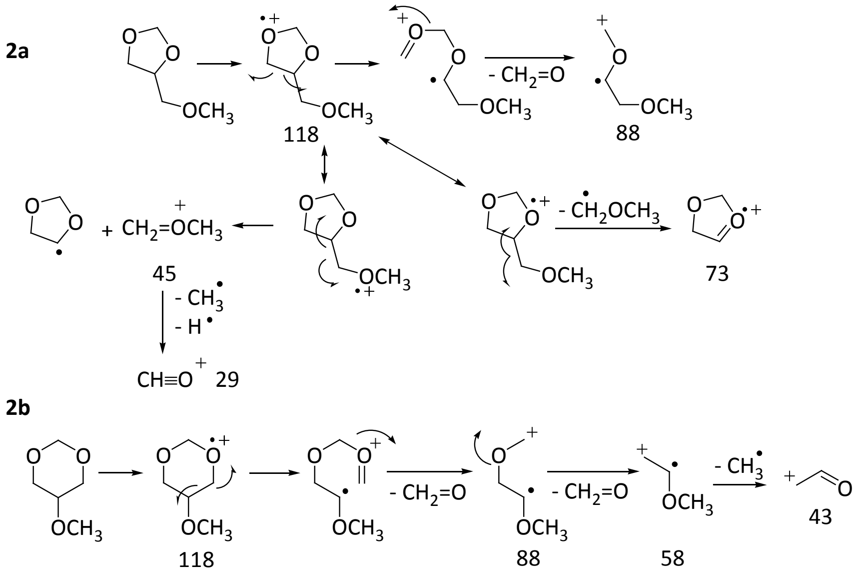


Figure 3. MS spectra of **2b** product.

GC/MS (relative intensity, 70 eV) m/z: 118 ($[M]^+$, 2%), 88 ($[M-H_2CO]^+$, 11), 58 ($[M-(H_2CO)_2]^+$, 100), 43 ($[M-(H_2CO)_2-CH_3]^+$, 34), 31 (14), 29 (30), 28 (20).

Fragmentation pathways for compounds **2a** and **2b** are illustrated in Scheme 1. These have been also obtained by comparison with literature data.[3]



Scheme 1. Fragmentation pathways for **2a-2b** products.

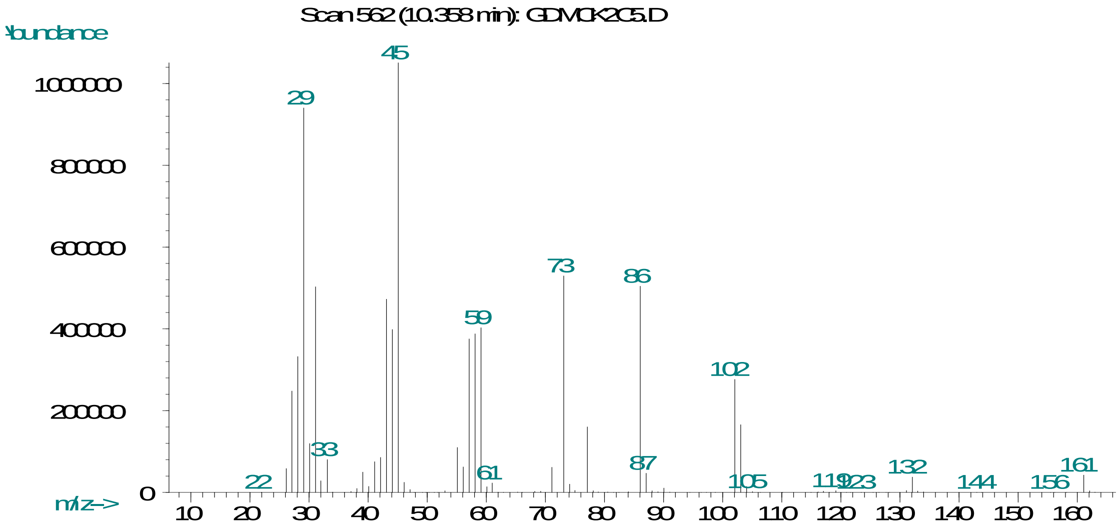


Figure 4. MS spectra of **3a** product.

GC-MS (relative intensity, 70 eV) m/z: 162 (M^+, <1%), 161 ($[M-H]^+$, 4), 103 ($[M-CO_2CH_3]^+$, 14), 102 (34), 86 ($[M-H-OCO_2CH_3]^+$, 49), 77 (14), 73 ($[M-CH_2OCO_2CH_3]^+$, 44), 59 ($[CH_3OC{\equiv}O]^+$, 40), 58 (43), 57 (38), 55 (11), 45 ($[CH{=}OCH_3]^+$, 100), 44 (36), 43 (50), 31 (52), 30 (10), 29 ($[CH{\equiv}O]^+$, 98), 28 (34), 27 (25).

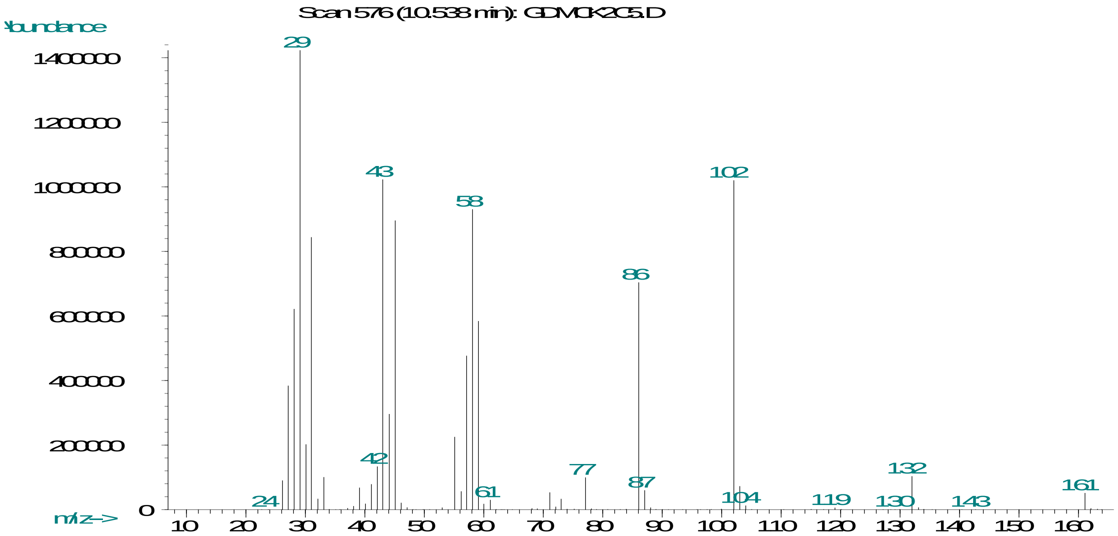


Figure 5. MS spectra of **3b** product.

GC-MS (relative intensity, 70 eV) m/z: 162 (M^+, <1%), 161 ($[M\text{-}H]^+$, 4%), 102 ($[M\text{-}(H_2CO)_2]^+$, 72), 86 ($[M\text{-}H\text{-}CO_2\text{-}OCH_3]^+$, 49), 59 ($[CH_3OC{\equiv}O]^+$, 41), 58 ($[M\text{-}(H_2CO)_2\text{-}CO_2]^+$, 65), 57 (33), 55 (16), 45 (63), 44 (21), 43 ($[M\text{-}(H_2CO)_2\text{-}CO_2CH_3]^+$, 72), 31 (59), 30 (14), 29 ($[CH{\equiv}O]^+$,100), 28 (44), 27 (27).

References

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[2] M. Selva, C. A. Marques, P. Tundo, J. Chem. Soc., Perkin Trans. I, 1995, 1889-1893.

[3] E. De Hoffman, J. Charette, V. Stroobant, In Mass Spectrometry, Principles and Applications, J. Wiley & Sons, 1996.