

Palladium-catalyzed synthesis of 2,3-dihydro-2-substituted-2-vinyl-1,4-benzodioxins

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Dedicated to Professor Marcial Moreno-Mañas on the occasion of his 60th birthday

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Abstract

Various 2,3-dihydro-2-substituted-2-vinyl-1,4-benzodioxins **6** are obtained by alkylation of the methyl carbonate of 2,3-dihydro-1,4-benzodioxin-2-ylideneethanol **5** with various carbon nucleophiles in the presence of a palladium complex. Although the yields in alkylation products are good in the case of a non-bulky nucleophile, formation of the diene **7** was generally observed when a bulky nucleophile was used.

Keywords: Substituted 2-vinyl-benzodioxins, condensation, palladium, alkylation

Introduction

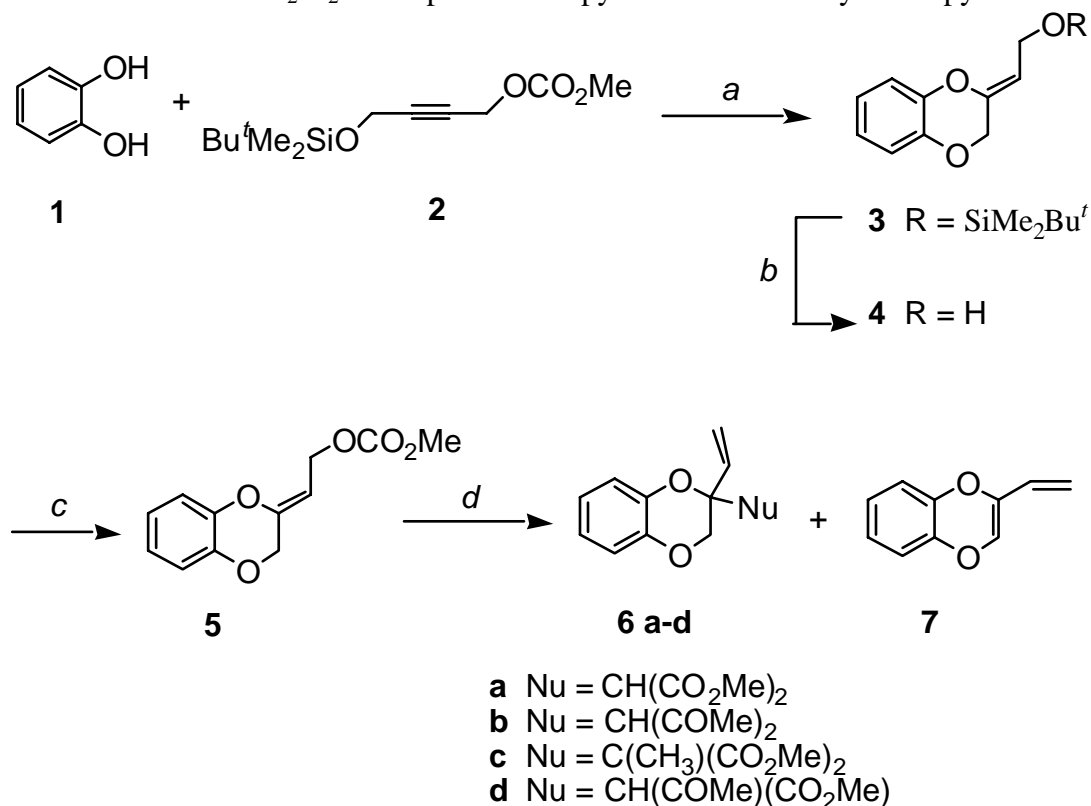
Compounds containing 1,4-benzodioxin and 1,4-benzodioxan structures have attracted considerable interest in recent years. This is mainly due to the interesting properties of these compounds. Some of them act as α - or β -blocking agents and could be used in antidepressant or antihypertension therapy.¹⁻⁵ Others have antihyperglycemic properties⁶ or act as inhibitors of 5-lipoxygenase.⁷ The 1,4-benzodioxan frame is also found in a variety of biological active natural products.⁸⁻¹¹ It is also to be noticed that these compounds are useful intermediates in a variety of synthetic transformations.¹²⁻¹⁴

There are many approaches for the synthesis of substituted 1,4-benzodioxins,¹⁵⁻²⁰ even in an asymmetric way.^{20,21} We have recently described the preparation of various 2,3-dihydro-2-ylidene-1,4-benzodioxins *via* a palladium-catalyzed condensation of benzene-1,2-diol with different propargylic carbonates.²² Among the prepared heterocyclic compounds, we expected that *tert*-butyldimethyl-[(2,3-dihydro-1,4-benzodioxin-2-ylidene)ethoxy]silane **3**, obtained by palladium condensation of benzene-1,2-diol **1** with propargylic carbonate **2**, could be a valuable

starting material for the preparation of 2,3-dihydro-2-substituted-2-vinyl-1,4-benzodioxins. We described in this paper preliminary results in this field.

Results and Discussion

Cyclization of benzene-1,2-diol **1** with carbonate **2**²³ was performed in THF at room temperature in the presence of 2.5 mol% Pd₂(dba)₃ and 10 mol % dppb or 1,4-bis(diphenylphosphino)butane to afford after column chromatography 2,3-dihydro-1,4-benzodioxin derivative **3** in 67% yield (Scheme 1). Desilylation of compound **3** performed in THF as the solvent in the presence of tetrabutylammonium bromide trihydrate gave 2,3-dihydro-1,4-benzodioxin-2-ylideneethanol **4** in 95% yield after column chromatography. Carbonate **5** was obtained in 95% yield after column chromatography by condensation of this alcohol **4** with methyl chloroformate in CH₂Cl₂ in the presence of pyridine and dimethylaminopyridine.



(a) Pd₂(dba)₃, THF, 20 h; (b) Bu₄NBr·3H₂O, THF; (c) ClCO₂Me, DMAP, C₅H₅N, CH₂Cl₂; (d) Pd₂(dba)₃, NuH, THF.

Scheme 1

The reaction of various nucleophiles with this carbonate **5** was performed in THF at room temperature in the presence of 2.5 mol % Pd₂(dba)₃ and 10 mol % dppb. The results are summarized in Table 1.

Table 1. Palladium-catalyzed reaction of NuH with allylic carbonate **5**

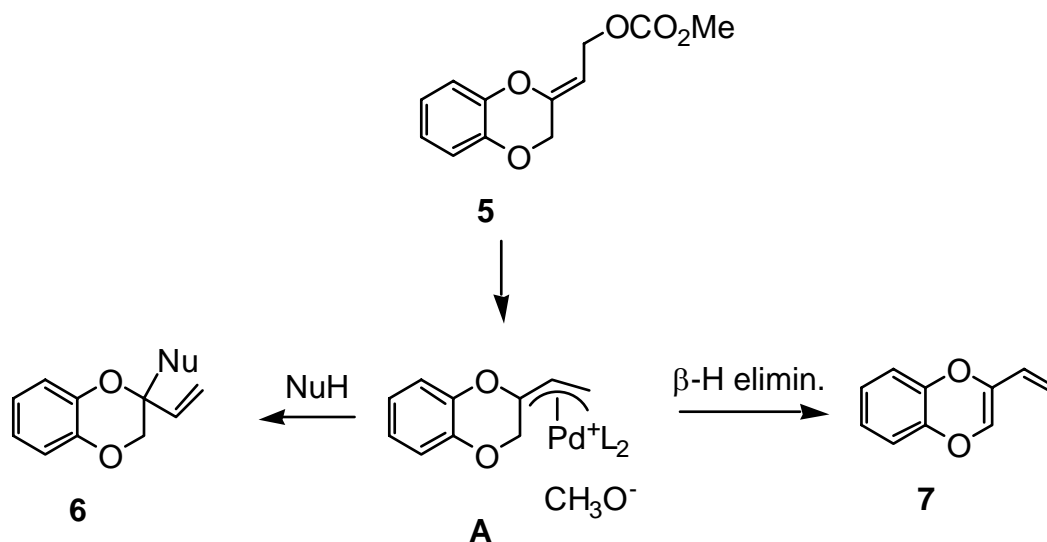
Entry	Nucleophile NuH	Yield % compound 6	Yield % compound 7
1	CH ₂ (CO ₂ CH ₃) ₂	67	11
2	CH ₂ (COCH ₃) ₂	53	33
3	CH(CH ₃)(CO ₂ CH ₃) ₂	6	15
4	CH ₂ (COCH ₃)(CO ₂ C ₂ H ₅)	61	18
5	C(NHCOCH ₃)(CO ₂ CH ₃) ₂	0	24

Dimethyl malonate (Table 1, entry 1) and acetylacetone (Table 1, entry 2) reacted with carbonate **5** to give after column chromatography the alkylated 2,3-dihydro-2-vinyl-benzo-1,4-dioxins **6a** and **6b** in 67 and 53% yield, respectively. The formation of 2-vinylbenzo-1,4-dioxine **7** was also observed in 11 and 33% yield, respectively. When dimethyl methylmalonate was used as the nucleophile (Table 1, entry 3), the formation of the alkylated compound **6c** was observed in quite low yield (6%) together with diene **7** (15%). The use of dimethyl acetamidomalonate as the nucleophile (Table 1, entry 5) afforded only the unsaturated compound **7** in 24% yield, with no trace of the corresponding alkylated compound.

Finally reaction of carbonate **5** with ethyl acetoacetate as the nucleophile gave the alkylated product **6d** in 61% yield as a mixture of the two diastereoisomers in a ratio 66:34, together with the diene **7** in 18% yield (Table 1, entry 4).

The formation of compounds **6** and **7** could be explained according to Scheme 2. The first step is the formation of the η^3 -allyl intermediate **A** by oxidative addition of the palladium complex on compound **5**. One possibility is the generation of the nucleophile by abstraction of a hydrogen from Nu-H by CH₃O⁻. The attack of the nucleophile on the η^3 -allyl intermediate **A** occurred not at the less hindered termini, but at the more electrophilic termini of this intermediate affording compound **6** bearing a quaternary carbon center. This regioselectivity is in agreement with previous studies on η^3 -allyl intermediates bearing an oxygen atom on one of the termini of the η^3 -allyl system.²⁴⁻²⁶ It is to be noticed that this alkylation reaction is very sensitive to the bulkiness of the nucleophile; the more bulky the nucleophile is (dimethyl methylmalonate, dimethyl acetamidomalonate), the lowest is the chemical yield in the alkylated product.

The formation of the diene **7** could be explained by a β -hydrogen elimination from the intermediate **A**, leading to compound **7** and the formation of H(CH₃O)Pd(dppb), affording Pd(dppb) *via* a reductive elimination of CH₃OH.²⁷ It seems that there is a competition between these two pathways.



Scheme 2

Mechanism of formation of compounds **6** and **7**

Conclusions

In conclusion, we have shown that various 2,3-dihydro-2-substituted-2-vinyl-1,4-benzodioxins **6** bearing a quaternary carbon could be very easily obtained from *tert*-butyldimethyl-[(2,3-dihydro-1,4-benzodioxin-2-ylidene)ethoxy]silane **4** via a palladium-catalyzed alkylation reaction of the corresponding carbonate with various carbon-nucleophiles. However the chemical yields are strongly dependent on the bulkiness of the nucleophile, with the preferential formation of a diene when this nucleophile is too bulky. Work is actually in progress in our group in order to prepare chiral 2,3-dihydro-2-substituted-2-vinyl-1,4-benzodioxins **6** via the use of chiral ligands.

Experimental Section

General Procedures. All manipulations involving palladium catalysis were performed in Schlenk tubes under a nitrogen atmosphere. Unless otherwise stated, the materials were commercial samples; propargylic carbonate **2** was prepared as previously described.²³ All organic solvents were of analytical quality and used as purchased. Solvents mixtures are defined by volume ratios (v/v). Tetrahydrofuran was distilled from sodium/benzophenone. All ¹H- and ¹³C-NMR spectra were recorded on a Brücker AM 300 spectrometers in CDCl₃. Chemical shifts are reported on the δ scale with the reference to tetramethylsilane or CDCl₃ as the internal standard and the coupling constants *J* are given in Hz. The IR-spectra were recorded on a Perkin-Elmer 681 instrument. Tin-layer chromatography was performed using Merck silica gel 60 F₂₅₄ precoated aluminium plates, 0.2 mm thickness. Visualisation was by UV or by spraying

with 10% sulphuric acid and then heating. Column chromatography was carried out using Merck silica gel (Kieselgel 60, 70–230 mesh).

(Z)-tert-Butyldimethyl-[(2,3-dihydro-1,4-benzodioxin-2-ylidene)ethoxy]silane (3). A mixture of Pd₂(dba)₃ (20.8 mg, 2.2 × 10⁻² mmol), in THF (7 mL), was stirred under a nitrogen atmosphere at room temperature for 30 min. This catalyst solution was added to a mixture of benzene-1,2-diol **1** (100 mg, 0.9 mmol) and carbonate **2** (284 mg, 1.1 mmol). The resulting solution was stirred at room temperature for 24 h. The solvent was evaporated and the residue chromatographed over silica (*R_f* = 0.24, petroleum ether/EtOAc 100:1) to give 196 mg of **3** as an oil (yield 67%); ¹H-NMR δ 7.10–6.80 (4H, m, H_{arom}), 4.91 (1H, t, *J* = 6.3, =CH-CH₂), 4.47 (2H, s, 3-H), 4.47 (2H, d, *J* = 6.3, =CH-CH₂), 0.88 (9H, s, CH₃), 0.12 (6H, s, CH₃); ¹³C-NMR δ 144.0 (2-C), 143.2 (C_{arom}), 142.6 (C_{arom}), 122.3 (C_{arom}), 122.2 (C_{arom}), 117.4 (C_{arom}), 116.6 (C_{arom}), 107.7 (=CH-CH₂), 65.1 (3-C), 56.6 (CH₂OSi), 26.1 (CMe₃), 18.4 (CMe₃), -5.1 (SiMe); IR ν 3060, 3040, 2950, 2920, 2880, 2850, 1690, 1590, 1480, 1460, 1250 cm⁻¹. Anal. Calcd for C₁₆H₂₄O₃Si: C, 65.72; H, 8.28. Found: C, 65.39; H, 8.61.

(Z)-2,3-Dihydro-1,4-benzodioxin-2-ylideneethanol (4). A solution of compound **3** (2.57 g, 9 mmol) and Bu₄NBr·3H₂O (4.60 g, 18 mmol) in tetrahydrofuran (80 mL) was stirred at 25 °C for 1 h. After evaporation of the solvent, the residue was diluted with diethyl ether (100 mL), and the ethereal solution was washed three times with a saturated aqueous solution of sodium chloride (3×40 mL), and dried over sodium sulfate. Chromatography (*R_f* = 0.24, petroleum ether/EtOAc 4:3) of the residue obtained after evaporation of the solvent gave 1.49 g of compound **4** (yield 95%); oil; ¹H-NMR δ 7.10–6.80 (4H, m, H_{arom}), 4.93 (1H, t, *J* = 7.0, =CH-CH₂), 4.44 (2H, s, 3-H), 4.38 (2H, d, *J* = 7.0, =CH-CH₂), 2.65 (1H, bs, OH); ¹³C-NMR δ 144.5 (2-C), 143.9 (C_{arom}), 142.4 (C_{arom}), 122.5 (C_{arom}), 122.4 (C_{arom}), 117.4 (C_{arom}), 116.6 (C_{arom}), 106.7 (=CH-CH₂), 65.9 (3-C), 56.8 (CH₂OH); IR ν 3350, 3060, 3040, 2940, 2920, 2850, 1690, 1590, 1490, 1250 cm⁻¹. These values are in agreement with the literature.²⁸

Carbonic acid (Z)-(2-benzo[1,4]dioxin-2-ylidenethyl) ester methyl ester (5). To a stirred solution of the alcohol **4** (360 mg, 2 mmol), dimethylaminopyridine (50 mg, 0.4 mmol), and pyridine (632 mg, 8 mmol), in CH₂Cl₂ (10 mL) at 0 °C under argon was slowly added methyl chloroformate (756 g, 8 mmol). After being stirred for 24 h at room temperature, the solution was hydrolyzed with a saturated aqueous solution of copper sulfate (10 mL), and extracted three times with diethyl ether (3×20 mL). The ethereal solution was washed with a saturated aqueous solution of copper sulfate (10 mL), and dried over sodium sulfate. Evaporation of the solvent followed by column chromatography (*R_f* = 0.66, petroleum ether/EtOAc 4:1) of the residue gave 448 mg of compound **5** as an oil (yield 95%); ¹H-NMR δ 7.10–6.80 (4H, m, H_{arom}), 5.00–4.87 (3H, m, =CH-CH₂, =CH-), 4.45 (2H, s, 3-H), 3.80 (3H, s, CH₃); ¹³C-NMR δ 155.8 (CO), 147.0 (2-C), 143.9 (C_{arom}), 142.2 (C_{arom}), 122.7 (C_{arom}), 122.4 (C_{arom}), 117.4 (C_{arom}), 116.7 (C_{arom}), 100.7 (=CH-CH₂), 64.8 (3-C), 61.0 (=CH₂CH₂O), 54.8 (CH₃); IR ν 3060, 3040, 3020, 2990, 2950, 2890, 2850, 1750, 1690, 1590, 1490, 1450, 1250 cm⁻¹. Anal. Calcd for C₁₂H₁₂O₅: C, 60.00; H, 5.12. Found: C, 60.63; H, 5.16.

Alkylation of carbonic acid (Z)-(2-benzo[1,4]dioxin-2-ylidenethyl) ester methyl ester. To a stirred solution of carbonate **5** (104 g, 0.44 mmol) and nucleophile (0.53 mmol) in THF (7 mL) at 25 °C under argon was added the catalyst solution obtained by stirring under argon for 0.5 h $\text{Pd}_2(\text{dba})_3$ (10.4 mg, 1.1×10^{-2} mmol) and dppb (19.4 mg, 4.6×10^{-2} mmol) in THF (7 mL). After being stirred for 24 h at room temperature, the solvent was evaporated and the residue purified by column chromatography to give the alkylated compound **6**.

2-(2,3-Dihydro-2-vinyl-1,4-benzodioxin-2-yl)malonic acid dimethyl ester (6a). Oil; yield 69%; $R_f = 0.20$ (petroleum ether/AcOEt 15:1); $^1\text{H-NMR}$ δ 7.00–6.80 (4H, m, H_{arom}), 6.26 (1H, dd, $J = 17.3, 11.0$, $-\text{CH}=\text{}$), 5.49 (1H, dd, $J = 17.3, 0.7$, $=\text{CH}_2$), 5.38 (1H, dd, $J = 11.0, 0.7$, $=\text{CH}_2$), 4.56 (1H, d, $J = 11.4$, 3-H), 4.15 (1H, d, $J = 11.4$, 3-H), 4.01 (1H, s, $-\text{CH}<$), 3.76 (3H, s, CH_3), 3.72 (3H, s, CH_3); $^{13}\text{C-NMR}$ δ 166.9 (CO), 166.5 (CO), 142.5 (C_{arom}), 141.7 (C_{arom}), 133.6 ($-\text{CH}=\text{}$), 122.2 (C_{arom}), 121.8 (C_{arom}), 118.9 ($=\text{CH}_2$), 117.7 (C_{arom}), 117.2 (C_{arom}), 76.1 (2-C), 68.1 (3-C), 55.5 ($-\text{CH}<$), 52.8 (CH_3), 52.6 (CH_3); IR ν 3080, 3040, 3020, 2950, 2920, 2870, 2840, 1750, 1645, 1595, 1490, 1430, 1255 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_6$: C, 61.62; H, 5.52. Found: C, 61.89; H, 5.55.

3-(2,3-Dihydro-2-vinyl-1,4-benzodioxin-2-yl)pentane-2,4-dione (6b). Oil; yield 53%; $R_f = 0.24$ (petroleum ether/AcOEt 10:1); $^1\text{H-NMR}$ δ 7.00–6.80 (4H, m, H_{arom}), 6.25 (1H, dd, $J = 17.3, 11.0$, $-\text{CH}=\text{}$), 5.51 (1H, dd, $J = 17.3, 1.1$, $=\text{CH}_2$), 5.35 (1H, dd, $J = 11.0, 1.1$, $=\text{CH}_2$), 4.36 (1H, d, $J = 11.6$, 3-H), 4.30 (1H, s, $-\text{CH}<$), 3.95 (1H, d, $J = 11.6$, 3-H), 2.29 (3H, s, CH_3), 2.21 (3H, s, CH_3); $^{13}\text{C-NMR}$ δ 202.9 (CO), 202.7 (CO), 143.0 (C_{arom}), 141.6 (C_{arom}), 133.8 ($-\text{CH}=\text{}$), 122.8 (C_{arom}), 122.4 (C_{arom}), 118.9 ($=\text{CH}_2$), 118.0 (C_{arom}), 117.8 (C_{arom}), 77.5 (2-C), 69.2 (3-C), 68.0 ($-\text{CH}<$), 32.8 (CH_3), 32.5 (CH_3); IR ν 3080, 3030, 2990, 2950, 2910, 2870, 1720, 1640, 1590, 1490, 1460, 1250 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_4$: C, 69.20; H, 6.20. Found: C, 69.43; H, 6.22.

2-(2,3-Dihydro-2-vinyl-1,4-benzodioxin-2-yl)-2methylmalonic acid dimethyl ester (6c). Oil; yield 6%; $R_f = 0.30$ (petroleum ether/AcOEt 15:1); $^1\text{H-NMR}$ δ 7.30–6.80 (4H, m, H_{arom}), 6.07 (1H, dd, $J = 17.1, 10.9$, $-\text{CH}=\text{}$), 5.29 (1H, dd, $J = 10.9, 1.0$, $=\text{CH}_2$), 5.20 (1H, dd, $J = 17.1, 1.0$, $=\text{CH}_2$), 4.80 (1H, d, $J = 11.2$, 3-H), 4.32 (1H, d, $J = 11.2$, 3-H), 3.73 (3H, s, CH_3), 3.71 (3H, s, CH_3), 3.09 (3H, s, CH_3); IR ν 3040, 2950, 2880, 1750, 1645, 1600, 1450, 1430, 1255 cm^{-1} .

2-(2,3-Dihydro-2-vinyl-1,4-benzodioxin-2-yl)-3-oxobutyric acid methyl ester (6d). As an oily mixture of two diastereoisomers 66:34; yield 61%; $R_f = 0.30$ (petroleum ether/AcOEt 15:1); $^1\text{H-NMR}$ δ 6.96–6.86 (4H, m, H_{arom}), 6.32 (0.66H, dd, $J = 17.2, 11.1$, $-\text{CH}=\text{}$), 6.18 (0.34H, dd, $J = 17.3, 10.9$, $-\text{CH}=\text{}$), 5.52 (0.66H, dd, $J = 17.2, 1.1$, $=\text{CH}_2$), 5.45 (0.34H, dd, $J = 17.3, 1.1$, $=\text{CH}_2$), 5.39 (0.66H, dd, $J = 11.1, 1.1$, $=\text{CH}_2$), 5.34 (0.34H, dd, $J = 10.9, 1.1$, $=\text{CH}_2$), 4.50 (0.66H, d, $J = 11.5$, 3-H), 4.37 (0.34H, d, $J = 11.5$, 3-H), 4.28 (0.34H, d, $J = 11.5$, 3-H), 4.26–4.15 (2H, m, OCH_2CH_3), 4.09 (0.66H, s, $-\text{CH}<$), 4.06 (0.34H, s, $-\text{CH}<$), 3.96 (0.66H, d, $J = 11.5$, 3-H), 2.33 (3H, s, CH_3), 2.24 (3H, s, CH_3), 1.26 (1.98H, t, $J = 7.1$, CH_3), 1.25 (1.02H, t, $J = 7.1$, CH_3); $^{13}\text{C-NMR}$ δ 201.7 (CO), 143.0 (C_{arom}), 142.1 (0.34 C_{arom}), 141.7 (0.66 C_{arom}), 134.5 (0.34 $-\text{CH}=\text{}$), 133.5 (0.66 $-\text{CH}=\text{}$), 122.8 (0.66 C_{arom}), 122.5 (0.34 C_{arom}), 122.4 (0.66 C_{arom}), 122.1 (0.34 C_{arom}), 119.1 (0.66 $=\text{CH}_2$), 119.0 (0.34 $=\text{CH}_2$), 118.1 (0.66 C_{arom}), 117.9 (0.34 C_{arom}), 117.8 (0.66 C_{arom}), 117.6 (0.34 C_{arom}), 77.2 (0.34 2-C), 76.9 (0.66 2-C), 69.4 (0.66 3-C), 68.2 (0.34 3-C), 62.1 (0.34

OCH₂CH₃), 62.0 (0.66 OCH₂CH₃), 63.2 (0.34 -CH<), 61.4 (0.66 -CH<), 32.3 (0.66 CH₃), 32.2 (0.34 CH₃), 14.4 (CH₃); IR ν 3080, 3040, 2980, 2930, 2880, 1745, 1715, 1595, 1490, 1255 cm⁻¹. Anal. Calcd for C₁₆H₁₈O₅: C, 66.18; H, 6.25. Found: C, 66.01; H, 6.32.

2-Vinyl-1,4-benzodioxin (7). R_f = 0.85 (petroleum ether/AcOEt 15:1); ¹H-NMR δ 6.90–6.30 (4H, m, H_{arom}), 5.95 (1H, bs, 3-H), 5.90 (1H, dd, J = 17.0, 11.0, -CH=), 5.42 (1H, dd, J = 17.0, 0.8, =CH₂), 5.02 (1H, dd, J = 11.0, 0.8, =CH₂); IR ν 3040, 2950, 2880, 1750, 1645, 1600, 1490, 1430, 1255 cm⁻¹. These values are in agreement with those published in the literature.¹²

Acknowledgements

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