

Short Note

1,4-Di(2-butoxycarbonyl-*trans*-vinyl)-2,5-dimethoxybenzene

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Academic Editor: Norbert Haider

Received: 8 September 2015 / Accepted: 5 November 2015 / Published: 23 November 2015

Abstract: The title compound 1,4-di(2-butoxycarbonyl-*trans*-vinyl)-2,5-dimethoxybenzene was synthesized in 94% yield through the Heck reaction between 2,5-diiodo-1,4-dimethoxybenzene and *n*-butyl acrylate, using bis(dibenzylideneacetone) palladium(0) as homogeneous catalyst.

Keywords: 1,4-di(2-butoxycarbonyl-*trans*-vinyl)-2,5-dimethoxybenzene; Heck reaction; triphenyl phosphite; *p*-divinylbenzene

1. Introduction

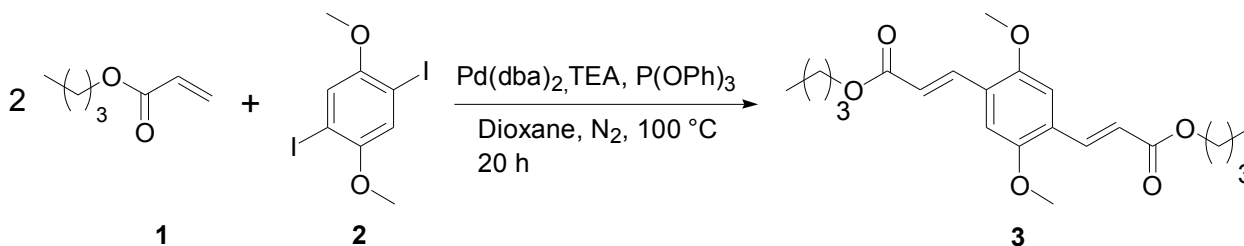
Divinylbenzene and its derivatives are a very interesting class of monomer templates for the preparation of oligomeric and polymeric materials with a wide range of technological possibilities. These useful polymers have many successful and promising applications in the production of copolymers [1–3], resins [4–6], membranes [7], electroluminescent devices [8,9], fluorescent sensors [10], fluorophores [11,12], dendrimers [13,14] and helicenenes [15].

p-Divinylbenzene compounds can be synthesized through different synthetic methodologies that include the Knoevenagel reaction [16–18], Wittig reaction [19], Heck reaction [20–22], Horner-Wadsworth-Emmons reaction [23], olefination of aldehydes [24,25] and others [26,27]. Unfortunately not all of these reactions provide an efficient method for the formation of pure *trans* isomers, which are the desired products for several applications. Among these remarkable reactions that provided pure *trans* products, the Heck reaction additionally allows the facile construction of

structures with numerous substituents on the aromatic ring due to its compatibility with most functional groups. Specifically, in this work we describe the synthesis of 1,4-di(2-butoxycarbonyl-*trans*-vinyl)-2,5-dimethoxybenzene, a novel para-divinylbenzene derivative using the Heck reaction.

2. Results and Discussion

For the preparation of **3**, the aryl dihalide **2** [28] was reacted with two equivalents of *n*-butyl acrylate **1** in dioxane under solvothermal conditions (Scheme 1). Bis(dibenzylideneacetone)palladium(0) (Pd(dba)₂), triphenyl phosphite and triethylamine were used as catalyst, ligand and base respectively. The reaction was monitored using thin layer chromatography. After the purification, the desired title compound **3** was isolated in 94% yield.



Scheme 1. Synthesis of 1,4-di(2-butoxycarbonyl-*trans*-vinyl)-2,5-dimethoxybenzene **3**.

The title compound was characterized by IR, ¹H-NMR, ¹³C-NMR and elemental analysis. As expected, the IR spectrum shows a strong absorption band at 1695 cm⁻¹ for the C=O stretching vibration. The proton NMR spectrum showed the following signals: a triplet at 0.96 ppm assigned to the CH₃ groups, two multiplets at 1.43 and 1.69 ppm assigned to four CH₂ groups, a singlet at 3.87 ppm assigned to OCH₃ protons, a triplet at 4.21 ppm assigned to OCH₂- groups, two doublets at 6.54 and 7.94 ppm corresponding to the vinyl protons with a coupling constant of 16.1 and 16.0 Hz respectively which confirms the *trans* configuration for the double bond, and a singlet at 7.02 ppm for the aromatic protons.

3. Experimental

3.1. General Information

Melting points, reported without correction, were measured using a Stuart SMP10 apparatus (Staffordshire, UK). The FT-IR spectra were obtained with a Shimadzu IR prestige 21 spectrophotometer (Columbia, MD, USA). ¹H and ¹³C NMR spectra were recorded with a Bruker AVANCE III system (Billerica, MA, USA) operating at 300 MHz, using residual (δ_H 7.26) and deuterated solvent (δ_C 77.0) peaks of CDCl₃ as reference standards. The elemental analysis was performed on a Thermo Scientific Flash 2000 CHNS/O analyzer (Waltham, MA, USA).

3.2. 1,4-Di(2-butoxycarbonyl-*trans*-vinyl)-2,5-dimethoxybenzene

A mixture of *n*-butyl acrylate **1** (262 μL, 3.22 mmol), 2,5-diiodo-1,4-dimethoxybenzene **2** (599.2 mg, 1.536 mmol) [28], Pd(dba)₂ (8.8 mg, 0.015 mmol), triphenyl phosphite (20 μL, 0.077 mmol) and triethylamine (471 μL, 3.38 mmol) in 2 mL of dioxane was placed in a 10 mL glass vial. The vial was

sealed, purged with nitrogen and stirred at 100 °C for 20 h. After cooling the mixture, 5 mL of water was added and the product was recovered by filtration. The solid was dissolved in CH₂Cl₂, eluted through celite to eliminate the remnant catalyst, and after evaporation of the solvent the product was finally purified by recrystallization from ethanol. The target molecule **3** (566.2 mg, 94%) was recovered as yellow crystals, m.p: 124–125 °C.

FT-IR (ATR): 2960, 2929, 1695, 1626, 1501, 1462, 1414, 1261, 1217, 1169, 1043 cm⁻¹.

¹H-NMR (300 MHz, CDCl₃) δ(ppm): 0.96 (t, *J* = 7.4 Hz, 6H, 2CH₃), 1.43 (m, 4H, 2CH₂), 1.69 (m, 4H, 2CH₂), 3.87 (s, 6H, 2OCH₃), 4.21 (t, *J* = 6.7 Hz, 4H, 2OCH₂), 6.54 (d, *J* = 16.1 Hz, 2H, =CHCO₂Bu), 7.02 (s, 2H, H-Ar), 7.94 (d, *J* = 16.0 Hz, 2H, ArCH=).

¹³C-NMR (300 MHz, CDCl₃) δ(ppm): 13.8 (2CH₃), 19.2 (2CH₂), 30.8 (2CH₂), 56.0 (2OCH₃), 64.5 (2OCH₂), 111.1 (C(-H) ring), 119.9 (=CHCO₂Bu), 126.0 (C(-C) ring), 139.0 (ArCH=), 152.5 (C(-O) ring), 167.3 (C=O).

Anal. calcd for C₂₂H₃₀O₆: C, 67.67; H, 7.74. Found: C, 68.35; H, 7.96.

Copies of the IR, ¹H, ¹³C-NMR spectra for compound **3** are available in the supplementary information.

Acknowledgments

Authors wish to thank the Universidad Nacional de Colombia for financial support.

Author Contributions

The authors WM, CS, CO-P designed, accomplished research and wrote the paper together. Finally, all authors read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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