molbank

MDPI

Short Note

Benzyl 2-((*E*)-Tosyliminomethyl)phenylcarbamate

Kwang Min Ko and Sung-Gon Kim *

Department of Chemistry, Kyonggi University, 154-42, Gwanggyosan-ro, Yeongtong-gu, Suwon 16227, Republic of Korea; minwin89@naver.com

* Correspondence: sgkim123@kyonggi.ac.kr; Tel.: +82-31-249-9631

Academic Editor: Norbert Haider

Received: 8 September 2016; Accepted: 11 October 2016; Published: 17 October 2016

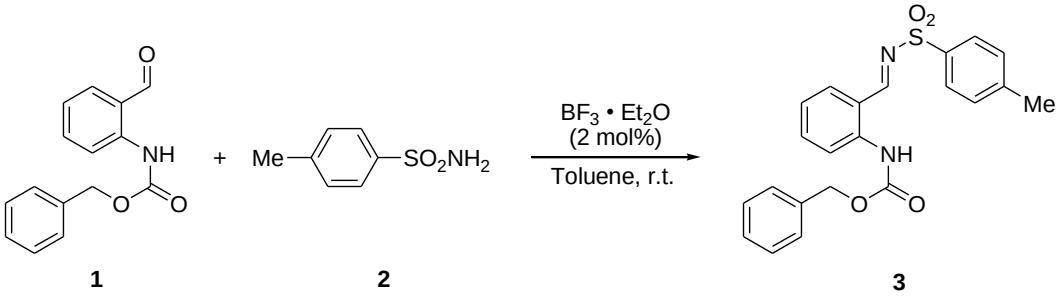
Abstract: Benzyl 2-((*E*)-tosyliminomethyl)penylcarbamate was prepared in good yield and characterized by the condensation reaction of benzyl 2-formylphenylcarbamate with *p*-toluenesulfonyl amine. The structure of the newly synthesized compound was determined using ^{1}H, ^{13}C-NMR, IR and mass spectral data.

Keywords: Schiff base; Imine; *p*-toluenesulfonyl amine; condensation reaction

1. Introduction

The Schiff base, structurally known as imine or azomethine, is a nitrogen analog of aldehyde or ketone in which the C=O group is replaced by C=N-R group after water molecular elimination [1]. Schiff bases are some of the most widely used organic compounds which used as pigments and dyes, catalysts and intermediates in organic synthesis [2]. Schiff bases have also been shown to exhibit a broad range of biological activities, including antibacterial, antimalarial, anti-inflammatory, antiviral, and anticancer properties [3–5]. In continuation of our research intefrest in 2-aminobenzaldehyde for the synthesis of highly functionalized chiral heterocylcles [6–9], we report here the preparation of a novel benzyl 2-((*E*)-tosyliminomethyl)phenylcarbamate.

The synthesis of the title compound **3** was achieved in one step, as presented in Scheme 1, which was performed by the condensation reaction of benzyl 2-formylphenylcarbamate (**1**) [10] with *p*-toluenesulfonyl amine (**2**). The reaction was carried out in toluene in the presence of 2 mol% of boron trifluoride diethyl etherate as a catalyst and provided the desired product in good yield. The structure of compound **3** was confirmed by ^{1}H- and ^{13}C-NMR, IR, mass spectral data, and all data are in accordance with the assumed structure.



Scheme 1. Synthesis of benzyl 2-((*E*)-tosyliminomethyl)penylcarbamate (**3**).

2. Experimental Section

2.1. General Information

All reagents were used as received without further purification. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator. Chromatographic purification of the title compound **3** was accomplished using forced-flow chromatography on ICN 60 32–64 mesh silica gel 63. Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Developed chromatograms were visualized by fluorescence quenching and anisaldehyde stain. ^{1}H and ^{13}C-NMR spectra were recorded on a 400 MHz instrument as noted, and were internally referenced to residual protio solvent signals. Data for ^{1}H-NMR were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C-NMR were reported in terms of chemical shift. IR spectra were recorded on Perkin-Elmer 1600 FT-IR spectrometer (Waltham, MA, USA), and reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectrometry data was recorded on a JEOL JMS-700 MStation mass spectrometer (JEOL, Tokyo, Japan).

*2.2. Syntheis of Benzyl 2-((E)-Tosyliminomethyl)penylcarbamate (**3**)*

p-Toluenesulfonyl amine (**2**, 94 mg, 0.55 mmol) was added to a solution of $BF_3{\cdot}Et_2O$ (1 μL, 0.01 mmol) and benzyl 2-formylphenylcarbamate (**1**, 128 mg, 0.50 mmol) in toluene (2 mL) at room temperature. The resulting mixture was refluxed for 60 h until complete consumption of benzyl 2-formylphenylcarbamate **1** was observed as determined by TLC. After being cooled to room temperature, water (2 mL) was added and the products were extracted with dichloromethane (3 × 5 mL). The organic phase was washed with aqueous saturated NaCl solution (2 × 5 mL), dried with anhydrous $MgSO_4$, and concentrated in vacuo. The crude residue was purified by flash silica gel column chromatography using EtOAc/hexane (1/10) as eluent to afford the desired title compound **3** (64%, 154 mg).

White solid; m.p. 158–160 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.83 (s, 1H), 9.02 (s, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 7.89–7.77 (m, 2H), 7.64–7.52 (m, 2H), 7.47–7.33 (m, 5H), 7.14 (ddd, *J* = 8.4, 6.9, 3.0 Hz, 3H), 5.20 (s, 2H), 2.39 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.38, 153.17, 144.79, 142.28, 137.27, 136.43, 135.96, 135.33, 129.87, 128.61, 128.35, 128.21, 127.78, 122.37, 118.76, 117.46, 67.11, 21.67; IR (film) 3248, 2923, 2855, 1735, 1597, 1562, 1537, 1447, 1376, 1317, 1222, 1162, 1088, 1067, 1067 cm^{-1}; HRMS (EI) *m*/*z* calcd for $[M]^+$ $C_{22}H_{20}N_2O_4S$: 408.1144 Found: 408.1158.

Supplementary Materials: ^{1}H- and ^{13}C-NMR spectra for compound **3** are available online at http://www.mdpi.com/1422-8599/2016/4/M912.

Acknowledgments: This work was supported by Kyonggi University's Graduate Research Assistantship 2016.

Author Contributions: Both authors contributed equally to this work.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Quin, W.; Long, S.; Panunzio, M.; Biondi, S. Schiff Bases: A short survey on an evergreen chemistry tool. *Molecules* **2013**, *18*, 12264–12289. [CrossRef] [PubMed]
2. Dhar, D.N.; Taploo, C.L. Schiff bases and their applications. *J. Sci. Ind. Res.* **1982**, *41*, 501–506.
3. Zoubi, W.A. Biological Activities of Schiff Bases and Their Complexes: A Review of Recent Works. *Int. J. Org. Chem.* **2013**, *3*, 73–95. [CrossRef]
4. Anand, P.; Patil, V.M.; Sharma, V.K.; Khosa, R.L.; Masand, N. Schiff bases: A review on biological insights. *Int. J. Drug Discov.* **2012**, *3*, 851–868.
5. Da Silva, C.M.; da Silva, D.L.; Modolo, L.V.; Alves, R.B.; de Resende, M.A.; Marins, C.V.B.; de Fátima, A. Schiff bases: A short review of their antimicrobial activities. *J. Adv. Res.* **2011**, *2*, 1–8. [CrossRef]

6. Lee, Y.; Heo, S.; Kim, S.-G. Asymmetric one-pot synthesis of 1,4-dihydroquinolines via an organocatalytic aza-Michael/Michael cascade strategy. *Adv. Synth. Catal.* **2015**, *357*, 1545–1550. [CrossRef]
7. Kim, H.; Kim, S.-G. One-pot organocatalytic enantioselective Michael addition and aza-cyclization/dehydration cascade reaction strategy: Asymmetric synthesis of highly functionalized 1,4-dihydroquinolines. *Tetrahedron Lett.* **2015**, *56*, 4819–4823. [CrossRef]
8. Yu, M.; Kim, S.-G. Asymmetric organocatalytic Michael addition/aza-cyclization coupled with sequential Michael addition for synthesizing densely polycyclic-fused dihydroquinolines. *Tetrahedron Lett.* **2015**, *56*, 4159–4162. [CrossRef]
9. Lee, Y.; Kim, S.-G. Asymmetric organocatalytic cascade reaction of aldehydes with 2-amino-β-nitrostyrenes: Synthesis of chiral tetrahydroquinolines and dihydroquinolines. *J. Org. Chem.* **2014**, *79*, 8234–8243. [CrossRef] [PubMed]
10. Wagner, A.M.; Knezevic, C.E.; Wall, J.L.; Sun, V.L.; Buss, J.A.; Allen, L.T.; Wenzel, A.G. A copper(II)-catalyzed, sequential Michael-aldol reaction for the preparation of 1,2-dihydroquinolines. *Tetrahedron Lett.* **2012**, *53*, 833–836. [CrossRef]