

Short Note

Dipropargyl 2,2'-isophthaloylbis(hydrazinecarboxylate)

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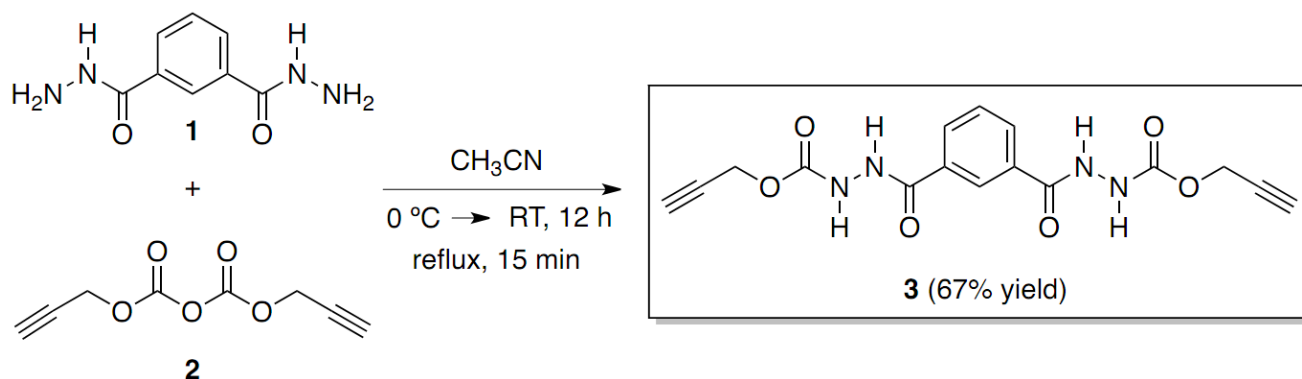
Abstract: The synthesis of dipropargyl 2,2'-isophthaloylbis(hydrazinecarboxylate) (**3**) by an addition-elimination reaction between isophthalic dihydrazide (**1**) and dipropargyl dicarbonate (**2**) is reported. The title compound was characterized by FT-IR, ¹H NMR, ¹³C NMR, EI-MS, elemental analysis and melting point determination.

Keywords: dicarbonate; alkyne; hydrazide; addition-elimination reaction

Substituted hydrazides have found important applications as traceless linkers for solid-phase synthesis [1] or as synthetic intermediates for the synthesis of pesticides [2], steroids [3], and antimycobacterials [4]. Taking advantage of their donor/acceptor hydrogen-bonding ability, hydrazides have been also used in the formation of molecular duplex strands via interstrand hydrogen bonds [5]. On the other hand, terminal alkynes are versatile functional groups in organic synthesis and materials science mainly due to their characteristic metal-catalyzed reactions [6]. In particular, polyvalent alkynes have emerged as valuable cross-linking agents and monomers in the renowned 'click' chemistry [7], with special emphasis on materials science [8,9].

Herein, we report the synthesis of dipropargyl 2,2'-isophthaloylbis(hydrazinecarboxylate) (**3**) by an addition-elimination reaction between isophthalic dihydrazide (**1**) and dipropargyl dicarbonate (**2**) in refluxing acetonitrile (Scheme 1). Symmetrical dipropargyl dicarbonate (**2**) was prepared from the corresponding propargyl chloroformate [10] following the method reported by Brown and co-workers [11].

Scheme 1.



Experimental Section

General

^1H and ^{13}C NMR spectra were recorded at $25\text{ }^\circ\text{C}$ on a Bruker Avance 300 spectrometer in CDCl_3 as solvent, and chemical shifts are reported relative to Me_4Si ($\delta = 0$) [10]. The low-resolution mass spectrum was obtained using a Varian MAT 311A spectrometer. Elemental analysis was performed on a Heraeus Mikro-Rapid analyzer. The infrared spectrum was recorded using a Diamond ATR (attenuated total reflection) accessory (Golden Gate) on a Bio-Rad Excalibur FTS 3000 MX spectrophotometer. The melting point (mp) was measured in a Büchi 510 and is uncorrected. Thin-layer chromatography was carried out on Merck aluminium sheets coated with silica gel 60 F₂₅₄. Compounds were visualized by use of 254 nm UV light and/or iodine as staining reagent. All solvents were of p.a. grade or purified by standard techniques [12]. Anhydrous sodium sulfate was used for drying solutions.

Synthesis of dipropargyl 2,2'-isophthaloylbis(hydrazinecarboxylate) (3): Dipropargyl dicarbonate (**2**) (500 mg, 2.75 mmol) in CH_3CN (5 mL) was added dropwise to isophthalic dihydrazide (**1**) (223 mg, 1.15 mmol) in CH_3CN (10 mL) at $0\text{ }^\circ\text{C}$ using an ice-water bath. The resulting mixture was vigorously stirred at room temperature for 12 h and further refluxed for 15 min. The solvent was evaporated under reduced pressure, and the residue was washed thoroughly with cold CH_3CN ($3 \times 10\text{ mL}$) and Et_2O ($3 \times 10\text{ mL}$). Further recrystallization from $\text{CH}_3\text{CN}/\text{MeOH}$ afforded compound **3** (276 mg, 67% yield) as an off-white hygroscopic solid: TLC R_f ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 4:1) 0.70; m.p. $204\text{--}206\text{ }^\circ\text{C}$; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ/ppm = 3.57 (s, 2 H), 4.74 (s, 4 H), 7.65 (t, $J = 7.6\text{ Hz}$, 1 H), 8.04 (dd, $J = 8.0\text{ Hz}$, 1.6 Hz, 2 H), 8.35 (s, 1 H), 9.53 (s, 2 H), 10.53 (s, 2 H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ/ppm = 52.3, 77.6, 78.8, 126.8, 128.8, 130.4, 132.6, 155.4, 165.4; FT-IR (ATR) ν_{max} (cm^{-1}) 3301, 3238, 3012, 1736, 1656, 1512; MS (ESI) m/z 359 [MH^+]. Elemental analysis calculated for $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_6 \cdot 1/3\text{ H}_2\text{O}$: C, 52.75; H, 4.06; N, 15.38; found: C, 52.60; H, 4.00; N, 15.62.

Acknowledgements

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