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 coworkers [11].
Experimental Section

General

$^1$H and $^{13}$C NMR spectra were recorded at 25 °C on a Bruker Avance 300 spectrometer in CDCl$_3$ as solvent, and chemical shifts are reported relative to Me$_4$Si ($\delta = 0$) [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 F$_{254}$. 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(hydrazonecarboxylate) (3): Dipropargyl dicarbonate (2) (500 mg, 2.75 mmol) in CH$_3$CN (5 mL) was added dropwise to isophthalic dihydrazide (1) (223 mg, 1.15 mmol) in CH$_3$CN (10 mL) at 0 °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$_3$CN (3 × 10 mL) and Et$_2$O (3 × 10 mL). Further recrystallization from CH$_3$CN/MeOH afforded compound 3 (276 mg, 67% yield) as an off-white hygroscopic solid: TLC $R_f$ (CH$_2$Cl$_2$/MeOH 4:1) 0.70; m.p. 204–206 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$/ppm = 3.57 (s, 2 H), 4.74 (s, 4 H), 7.65 (t, $J$ = 7.6 Hz, 1 H), 8.04 (dd, $J$ = 8.0 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, DMSO-$d_6$) $\delta$/ppm = 52.3, 77.6, 78.8, 126.8, 128.8, 130.4, 132.6, 155.4, 165.4; FT-IR (ATR) $\nu_{max}$ (cm$^{-1}$) 3301, 3238, 3012, 1736, 1656, 1512; MS (ESI) $m/z$ 359 [MH$^+$]. Elemental analysis calculated for C$_{16}$H$_{14}$N$_4$O$_6$·1/3 H$_2$O: C, 52.75; H, 4.06; N, 15.38; found: C, 52.60; H, 4.00; N, 15.62.

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References and Notes


10. See Supplementary Files.


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