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Short Note

1,1′,1″-(2′,4′-Dinitro-[1,1′-biphenyl]-2,4,6-triyl)tripiperidine

Gabriele Micheletti *, Dario Telese, Silvia Fazzini and Carla Boga *

Department of Industrial Chemistry "Toso Montanari", Alma Mater Studiorum-Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy; dario.telese2@unibo.it (D.T.); silvia.fazzini@studio.unibo.it (S.F.)

* Correspondence: gabriele.micheletti3@unibo.it (G.M.); carla.boga@unibo.it (C.B.); Tel.: +39-051-209-3641 (G.M.); +39-051-209-3616 (C.B.)

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Abstract: The compound 1,1′,1″-(2′,4′-dinitro-[1,1′-biphenyl]-2,4,6-triyl)tripiperidine was synthesized by S_EAr/S_NAr reaction between 1-fluoro-2,4-dinitrobenzene and 1,3,5-tris(*N*-piperidinyl)benzene. The structure of the newly synthesized compound was elucidated based on ^{1}H-NMR, ^{13}C-NMR, ESI-MS, UV-Vis and IR spectroscopy.

Keywords: S_NAr; S_EAr; 1,3,5-tris(*N*-piperidinyl)benzene; 1-fluoro-2,4-dinitrobenzene

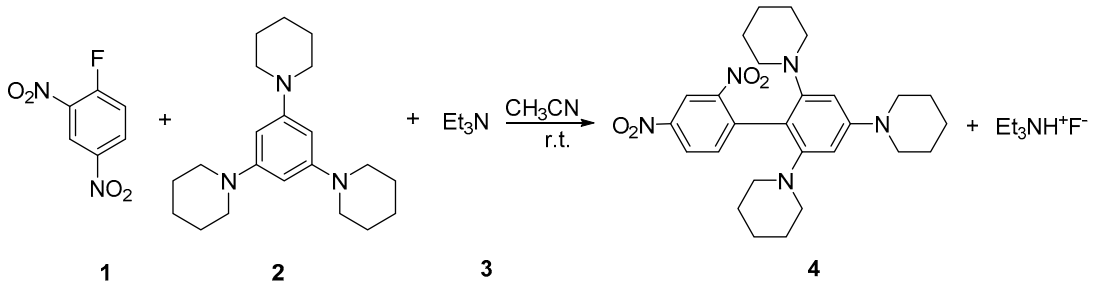
1. Introduction

Aromatic substitution reaction (both S_NAr [1,2] and S_EAr [3,4]) is one of the most important reactions in organic chemistry. In particular, the combination between aromatic electrophiles and nucleophiles at the neutral carbon atom allows one to obtain highly conjugated architectures bearing both electron donor and acceptor moieties. This kind of compound is receiving growing attention in material chemistry fields, such as solar energy conversion [5] and optoelectronic devices [6].

In the past, we reported several studies about this kind of reaction, mainly by coupling supernucleophiles such as 1,3,5-triaminobenzenes with different aromatic electrophiles [7–11]. Here, we report the synthesis of 1,1′,1″-(2′,4′-dinitro-[1,1′-biphenyl]-2,4,6-triyl)tripiperidine in mild conditions by the combination of 1-fluoro-2,4-dinitrobenzene (**1**) with 1,3,5-tris(*N*-piperidinyl)benzene (**2**). The product obtained may be of interest as a precursor for the hair-dyeing sector, since it is possible to reduce the two nitro groups to amino groups and to obtain a biphenyldiamine derivative. Notably, the molecules that belong to this class of compounds are known for their ability to react with the keratin present in the hair [12].

2. Results

The synthesis of 1,1′,1″-(2′,4′-dinitro-[1,1′-biphenyl]-2,4,6-triyl)tripiperidine (**4**) (Scheme 1) was performed by S_EAr/S_NAr reaction between 1-fluoro-2,4-dinitrobenzene (**1**) and 1,3,5-tripiperidinylbenzene (**2**) in acetonitrile at room temperature. The addition of triethylamine was made to prevent the protonation of reagent **2** by hydrofluoric acid, which is formed during the reaction course and would lead to a decrease in yield.



Scheme 1. Synthesis of 1,1′,1″-(2′,4′-dinitro-[1,1′-biphenyl]-2,4,6-triyl)tripiperidine.

At the end of the reaction, the product was purified by column chromatography on silica gel using a *n*-hexane/ethyl acetate ratio of 9/1 as eluent (yield 60%). The structure of the newly synthesized compound was elucidated based on ^{1}H-NMR, ^{13}C-NMR, ESI-MS, IR, and UV/Vis spectroscopy (see spectra in Supplementary Materials).

The reaction course follows the classic S_NAr mechanism; however, in reactions involving halonitrobenzenes, the ability of the latter to add nucleophiles is due to the activating effect of the nitro group, thus, nucleophiles should be able to add to these arenes also at positions occupied by hydrogen, subsequently resulting also in the formation of σ^H adducts [13]. This process is faster than the competing process of addition to the carbon atom bearing a nucleofugal group, resulting in the "classic" S_NAr reaction. Moreover, only when the σ^H adduct cannot be transformed into the S_NAr^H reaction product is the S_NAr reaction observed [14], as in the current case.

It must be noted that Effenberger [15] reported that the reaction between **2** and 1-chloro-2, 4-dinitrobenzene in 1:1 chloroform/ethanol at reflux did not occur. In the current case, the use of the more electrophilic fluoroderivative allowed us to obtain the novel compound, bearing contemporarily an electron donor and an electron acceptor moiety, which makes it of interest in the applied field as well as a potentially useful precursor in hair-dyeing technique.

3. Materials and Methods

The ^{1}H and ^{13}C spectra were recorded on a Mercury 400 (Varian, Palo Alto, CA, USA) spectrometer operating at 400 MHz (for ^{1}H-NMR) and at 100 MHz (for ^{13}C-NMR). Chemical shifts refer to the solvent for ^{1}H and ^{13}C-NMR ($\delta = 7.26$ ppm and $\delta = 77.0$ ppm, respectively, for $CDCl_3$). Signal multiplicities were established by Distortionless Enhanced by Polarization Transfer (DEPT) experiments. Chemical shifts were measured in δ (ppm). *J* values are given in Hertz. Electron spray ionization mass spectra (ESI-MS) were recorded with a WATERS ZQ 4000 instrument (Waters Corporation, Milford, MA, USA). IR spectrum were recorded with a Fourier transform spectrophotometer PerkinElmer FT-IR Spectrum Two (Perkin Elmer, Waltham, MA, USA) in the 4000−800 cm^{-1} wavelength range using a NaCl cell. UV/Vis spectrum was recorded using a Perkin Elmer Lamba 12 spectrophotometer. Chromatographic purifications (FC) were carried out on glass columns packed with Merck (Merck & Co. Readington, NJ, USA) silica gel (Merck grade 9385, 230−400 Mesh particle size, 60 Å pore size) at medium pressure. Thin layer chromatography (TLC) was performed on silica gel60 F_{254} coated aluminum foils (Fluka, Buchs, Switzerland).

The compound 1,3,5-Tris(*N*-piperidinyl)benzene was synthesized according to literature [11]; 1-fluoro-2,4-dinitrobenzene was purchased from Sigma-Aldrich (Milan, Italy).

Synthesis of 1,1′,1″-(2′,4′-Dinitro-[1,1′-biphenyl]-2,4,6-triyl)tripiperidine

In a round bottom flask, 1-fluoro-2,4-dinitrobenzene **1** (12.6 µL, 18.61 mg, 0.1 mmol) and 1,3,5-tris(*N*-piperidinyl)benzene **2** (32.7 mg, 0.1 mmol) were added and dissolved in acetonitrile (10 mL). Triethylamine (13.9 µL, 10.1 mg, 0.1 mmol) was added and the mixture was stirred at room temperature overnight. The reaction course was monitored by TLC (eluent hexane/ethyl acetate 9/1). The product

was purified by chromatography column on silica gel (eluent hexane/ethyl acetate 9/1). The product yield was 29.6 mg, 60%.

Dark red solid, cubic crystals (recrystallized from CH_3CN) m.p.: 240.4–241.2 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ, ppm: 8.81 (d, J = 2.4 Hz, 1H), 8.36 (dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz, 1H), 7.84 (d, J = 8.7 Hz, 1H), 6.42 (s, 2H), 3.22 (t, J = 5.6 Hz, 4H), 2.69–2.56 (m, 8H), 1.74–1.68 (m, 4H), 1.64–1.56 (m, 4,H), 1.40–1.27 (m, 10H); ^{13}C-NMR: (100 MHz, $CDCl_3$, 25 °C) δ, ppm: 153.9, 152.7, 149.1, 145.3, 140.8, 136.2 (CH), 125.5 (CH), 119.6 (CH), 116.1, 102.9 (CH), 53.2 (CH_2), 49.8 (CH_2), 25.9 (CH_2), 25.8 (CH_2), 24.3 (CH_2), 24.1 (CH_2); FT-IR υ (cm^{-1}): 3687, 3617, 320, 2398, 1942, 1598, 1524, 1432, 1224, 1208, 1046, 928; UV-Vis λ_{max} = 473 nm; ε_{473} = 4228 L mol^{-1} cm^{-1}; ESI-MS$^+$ (m/z): 494 $[M + H]^+$, 516 $[M + Na]^+$, 532 $[M + K]^+$; elemental analysis for $C_{27}H_{35}N_5O_4$, calculated C, 65.70; H, 7.15; N, 14.19; O, 12.96, found C, 65.73; H, 7.16; N, 14.17.

Supplementary Materials: The following are available online, Figure S1. ^{1}H-NMR spectrum in $CDCl_3$ of compound **4**; Figure S2. ^{13}C-NMR spectrum in $CDCl_3$ of compound **4**; Figure S3. DEPT spectrum in $CDCl_3$ of compound **4**; Figure S4. ESI-MS spectrum of compound **4**; Figure S5. FT-IR spectrum of compound **4**; Figure S6. UV/Vis spectrum of compound **4**.

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Conflicts of Interest: The authors declare no conflict of interest

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