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Synthesis of a Number of Unsymmetrical Bridged Terphthaloyl Acetophenone Oxime Esters

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Abstract

A number of unsymmetrical bridged terphthaloyl acetophenone oxime esters has been synthesized throughout an esterification reaction between four different acetophenone oximes and the terphthaloyl chloride in a molar ratio of (2:1) under mild basic conditions. Spectroscopic techniques, such as IR, HNMR and mass spectrometer, were used to confirm the structures of the targeted oxime esters. The yields of the obtained oxime esters ranged from 80% to 95%.

Keywords: Unsymmetrical; Bridged; Oxime esters; Esterification; Spectroscopic.

1. Introduction

Oximes and their esters could be found in many bioactive molecules. Oxime derivatives possess a wide variety of activities, such as antibacterial, antifungal, anti-inflammatory, antioxidant and cytotoxic activities [1]. Moreover, they have been utilized in the synthesis of photosensitive materials as important precursors and building blocks [2]. Oxime esters have importantly been considered as useful building units for the synthesis of nitrogen containing compounds such as amines, amides, nitriles, aliphatic heterocycles and aromatic heterocyclic compounds like pyrroles, pyridines, quinolones, etc [1, 2]. The chemical transformation of carbonyl compounds into oximes has intensively been considered for decades as an efficient method for the characterization and the purification of carbonyl compounds. Because of the nucleophilic character of oximes, they have widely been used for the synthesis of various nitrogen containing compounds such as amides, nitrones and nitriles [1]. The organic synthetic importance of some functional groups is due to their ability to be converted into oximes [3]. The oxime esters are considered as the most important oxime derivatives which showed a wide range of uses, such as anti-microbial, anti-inflammatory, fungicidal, antidepressant, antiulcer, analgesic, anti-HIV activities and their use in the production of agrochemicals [1-6]. Oxime esters are mainly useful for the photopolymerization of polymerizable compounds that consist of a C=C bond [7]. Herein, the synthesis of a number of unsymmetrical bridged terphthaloyl acetophenone oxime esters is described.

2. Experimental

2.1. Materials

The acetophenone oxime, 4-aminoacetophenone oxime, 4-hydroxyacetophenone oxime and the 4-nitroacetophenone oxime were obtained by following a literature procedure [8]. Terphthaloyl chloride, anhydrous sodium sulphate, triethyl amine and chloroform. These chemicals were P. K. Park and used without further purification.

2.2. Instrumentation

Melting points were measured on a Barnstead Electrothermal IA 9100. ^{1}HNMR spectrum was recorded on a JEOL ECA-300 II spectrometer. Residual proton signal from the deuteriated solvent was used as reference [DMSO (^{1}H, 2.50 ppm), whereas coupling constants were measured in hertz (Hz)]. Infrared spectrum was recorded on Jasco FT/IR-4100 Fourier transform infrared spectrometer. Mass spectrum was recorded on a Micromass Autospec M spectrometer.

2.3. Synthesis of 1-(*p*-Aminoacetophenone Oxime)-4-(Acetophenone Oxime) Phenyl Dicarboxylate 1

An adapted literature procedure [8] was followed to synthesize the oxime ester **1**. In a round-bottomed flask, a solution of terphthaloyl chloride (0.203 g, 1 mmol) in chloroform (50 cm^{3}) was added dropwise to a solution of the

acetophenone oxime (0.135 g, 1 mmol) in chloroform (20 cm^3) and in the presence of triethyl amine (0.252 g, 2.5 mmol) while stirring at 0 – 5 °C. The 4-aminoacetophenone oxime (0.150 g, 1 mmol) solution in chloroform (10 cm^3) was then added dropwise. The reaction mixture was left stirring for 1 hour at 0 – 5 °C and then the reaction was stirred at room temperature for 2 hours. A distilled water (30 cm^3) was added to the reaction mixture and stirred for further 10 min. The organic layer was extracted, dried over anhydrous Na_2SO_4 and filtered. The solvent was evaporated *in vacuo* to obtain the desired oxime ester **1** in a very good yield (0.334 g, 0.80 mmol, 80%) as an off-white solid. The product was recrystallized from diethyl ether. mp 175 – 177 ºC, IR ν_{max} (cm^{-1}) 3430 (NH_2) , 1732 (2 × C=O, ester), 1596 (C=N), 1406 (C=N). 1HNMR (DMSO-d6, 300 MHz) δ 7.90 (4H, d, *J* = 6.0, 4 × Ar-C*H*), 7.60 (4H, d, *J* = 6.0, 4 × Ar-C*H*), 7.40 – 7.30 (5H, m, 5 × Ar-C*H*), 4.43 (2H, br s, NH_2), 2.30 (3H, s, CH_3), 1.52 (3H, s, CH_3). Mass spec m/z ($C_{24}H_{21}N_3O_4$, MWt 415.45) 415 (27%), 400 (7%), 338 (17%), 149 (100%), 133 (7%), 123 (18%), 104 (38%), 77 (48%).

2.4. Synthesis of 1-(*p*-Hydroxyacetophenone Oxime)-4-(Acetophenone Oxime) Phenyl Dicarboxylate 2

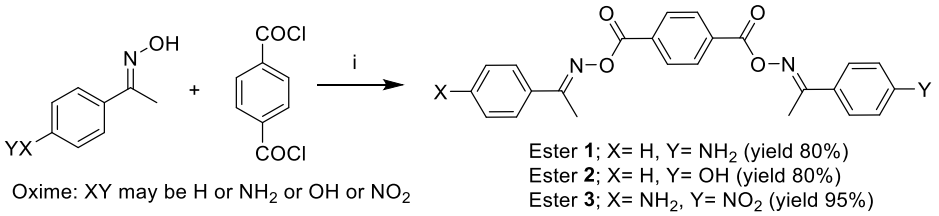
An adapted literature procedure [8] was followed to synthesize the oxime ester **2**. In a round-bottomed flask, a solution of terphthaloyl chloride (0.203 g, 1 mmol) in chloroform (50 cm^3) was added dropwise to a solution of the acetophenone oxime (0.135 g, 1 mmol) in chloroform (20 cm^3) and in the presence of triethyl amine (0.252 g, 2.5 mmol) while stirring at 0 – 5 °C. The 4-hydroxyacetophenone oxime (0.151 g, 1 mmol) solution in chloroform (10 cm^3) was then added dropwise. The reaction mixture was left stirring for 1 hour at 0 – 5 °C and then the reaction was stirred at room temperature for 2 hours. A distilled water (30 cm^3) was added to the reaction mixture and stirred for further 10 min. The organic layer was extracted, dried over anhydrous Na_2SO_4 and filtered. The solvent was evaporated *in vacuo* to obtain the desired oxime ester **2** in a very good yield (0.334 g, 0.80 mmol, 80%) as an off-white solid. The product was recrystallized from diethyl ether. mp 180 ºC, IR ν_{max} (cm^{-1}) 3320 (OH), 1732 (2 × C=O, ester), 1595 (C=N), 1406 (C=N). 1HNMR (DMSO-d6, 300 MHz) δ 9.15 (1H, s, O*H*), 7.98 (2H, d, *J* = 6.0, 2 × Ar-C*H*), 7.83 (2H, d, *J* = 6.0, 2 × Ar-C*H*), 7.60 (2H, d, *J* = 6.0, 2 × Ar-C*H*), 7.54 (2H, d, *J* = 6.0, 2 × Ar-C*H*), 7.39 – 7.27 (5H, m, 5 × Ar-C*H*), 2.29 (3H, s, CH_3), 1.39 (3H, s, CH_3). Mass spec m/z (C24H20N2O5, MWt 416.43) 416 (65%), 399 (10%), 312 (22%), 282 (9%), 266 (12%), 150 (100%), 134 (22%), 104 (48%), 77 (80%).

2.5. Synthesis of 1-(*p*-Aminoacetophenone Oxime)-4-(*p*-Nitroacetophenone Oxime) Phenyl Dicarboxylate 3

An adapted literature procedure [8] was followed to synthesize the oxime ester **3**. In a round-bottomed flask, a solution of terphthaloyl chloride (0.203 g, 1 mmol) in chloroform (50 cm^3) was added dropwise to a solution of the 4-nitroacetophenone oxime (0.180 g, 1 mmol) in chloroform (20 cm^3) and in the presence of triethyl amine (0.252 g, 2.5 mmol) while stirring at 0 – 5 °C. The 4-aminoacetophenone oxime (0.150 g, 1 mmol) solution in chloroform (10 cm^3) was then added dropwise. The reaction mixture was left stirring for 1 hour at 0 – 5 °C and then the reaction was stirred at room temperature for 2 hours. A distilled water (30 cm^3) was added to the reaction mixture and stirred for further 10 min. The organic layer was extracted, dried over anhydrous Na_2SO_4 and filtered. The solvent was evaporated *in vacuo* to obtain the desired oxime ester **3** in an excellent yield (0.437 g, 0.950 mmol, 95%) as an off-white solid. The product was recrystallized from diethyl ether. mp 220 ºC, IR ν_{max} (cm^{-1}) 3497 and 3397 (NH_2), 1740 (2 × C=O, ester), 1633 (C=N), 1433 (C=N), 1514 and 1348 (NO_2). ^{1}HNMR (DMSO-d6, 300 MHz) δ 8.20 – 7.90 (4H, m, 4 × Ar-CH), 7.70 – 7.60 (4H, m, 4 × Ar-CH), 7.55 – 7.40 (4H, m, 4 × Ar-CH), 4.25 (2H, br s, NH_2), 2.30 (3H, s, CH_3), 1.54 (3H, s, CH_3). Mass spec m/z ($C_{24}H_{20}N_4O_6$, MWt 460.45) 460 (15%), 327 (42%), 164 (14%), 149 (100%), 119 (16%).

3. Results and Discussion

The acetophenone oxime and 4-aminoacetophenone oxime or 4-hydroxyacetophenone oxime were reacted with the terphthaloyl chloride in the ratio of (2:1 mole/mole) under mild basic conditions at 0 °C to room temperature. The desired oxime esters **1** and **2** were obtained in a very good yields as an off-white solids. Similarly, when 4-aminoacetophenone oxime and 4-nitroacetophenone were reacted with the terphthaloyl chloride in the ratio of (2:1 mole/mole) under the same conditions, the oxime ester **3** was obtained in an excellent yield as an off-white solid **(Scheme 1)**.



Oxime: XY may be H or NH_2 or OH or NO_2

Ester **1**; X= H, Y= NH_2 (yield 80%)
Ester **2**; X= H, Y= OH (yield 80%)
Ester **3**; X= NH_2, Y= NO_2 (yield 95%)

Reagents & reaction conditions: (i) Et_3N, $CHCl_3$, 0 - 5 °C, 30 min, then rt, 2 hrs

Scheme 1: Synthesis of the Unsymmetrical Bridged Terphthaloyl Acetophenone Oxime Esters 1 – 3

The IR data revealed the presence of the imino group (C=N) in all obtained oxime esters **1 – 3** as two rather weak sharp absorption bands. The ^{1}HNMR data of the oxime esters **1** – **3** revealed the formation of these oxime

esters as all expected chemical shifts for all protons appeared in the spectra. The mass spectrometer further confirmed the formation of the oxime esters **1** – **3**. The molecular ion peaks for all synthesized oxime esters **1** – **3** were observed at 415, 416 and 460 m/z along with other molecular fragments that were in a line with the expected theoretical fragmentation patterns.

4. Conclusion

The synthesis of three unsymmetrical bridged terphthaloyl acetophenone oxime esters has been described. An esterification step between three acetophenone oximes and the terphthaloyl chloride under mild basic conditions led to the formation of the targeted three oxime esters **1 – 3**. The yields of the obtained oxime esters were ranging from 80% to 95%.

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