Academic Journal of Chemistry
ISSN(e): 2519-7045, ISSN(p): 2521-0211
Vol. 5, Issue. 6, pp: 55-57, 2020
URL: https://arpgweb.com/journal/journal/20
DOI: https://doi.org/10.32861/ajc.56.55.57

Academic Research Publishing Group

Original Research **Open Access**

Synthesis of Some Bridged Unsymmetrical Terphthaloyl Oxime Esters

Ramadan Ali Bawa (Corresponding Author)
Department of Chemistry, Faculty of Science, Misurata University, Libya
Email: ramadanali70@yahoo.com

Hana Mansoure Elmajdoub
Department of Chemistry, Faculty of Science, Misurata University, Libya

Article History
Received: May 20, 2020
Revised: June 14, 2020
Accepted: June 20, 2020
Published: June 23, 2020

Abstract

Three unsymmetrical bridged terphthaloyl acetophenone oxime esters have been synthesized throughout an esterification process between three acetophenone oximes and the terphthaloyl chloride under mild basic conditions. Spectroscopic techniques, such as IR, HNMR and mass spectrometer, were used to confirm the structures of the desired oxime esters. The yields of the resulting oxime esters ranged from 50% to 73%.

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

1. Introduction

Oximes and oxime esters could be found in many bioactive compounds. These compounds possess a vast range of activities, including antibacterial, antifungal, anti-inflammatory, antioxidant, anti- and cytotoxic activities [1]. They have also showed interesting insecticidal activities. Furthermore, they have been used as important precursors in the synthesis of photosensitive materials [2]. Oxime esters have been considered as important building blocks for the synthesis of nitrogen containing molecules such as amines, amides, nitriles, aliphatic heterocycles and aromatic heterocyclic compounds like pyrroles, pyridines, quinolones, etc [1, 2]. Transformation of carbonyl functionalities into oximes has attracted intensive attention in several decades as an efficient method for the characterization and purification of carbonyl compounds. Due to the nucleophilic character of oximes, they have been widely used for the preparation of a variety of nitrogen containing compounds such as amides, nitrones and nitriles [1]. Many functional groups are transformed into oximes that have made them very important in the synthetic organic chemistry [3]. The most important oxime derivatives are the oxime esters which possess a wide range of uses, including anti-microbial, anti-inflammatory, fungicidal, antidepressant, antiulcer, analgesic, anti-HIV activities; in addition to their use in the production of agrochemicals [1-6]. Oxime esters are particularly useful for the photopolymerization of a polymerizable compound having C=C bond [7].

2. Experimental

2.1. Materials

The acetophenone oxime 1, 4-methyl acetophenone oxime 2 and the 4-nitro acetophenone oxime 3 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-500 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-(Acetophenone Oxime)-4-(*p*-Nitroacetophenone Oxime) Diphenyl Carboxylate 4

An adapted literature procedure [8] was followed to synthesize the oxime ester **4**. In a round-bottomed flask, a solution of terphthaloyl chloride (2.03 g, 0.01 mmol) in chloroform (50 cm^3) was added dropwise to a solution of the acetophenone oxime **1** (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-nitroacetophenone oxime **3** (0.180 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 **4** in moderate yield (0.224 g, 0.50 mmol, 50%) as an off-white solid. The product was recrystallized from diethyl ether. mp 207 °C; IR ν_{max} (cm^{-1}) 1739 (2 × C=O, ester), 1693 (C=N), 1440 (C=N), 1519 and 1330 (NO_2). ^{1}HNMR (DMSO-d6, 300 MHz) δ 8.50 – 8.15 (5H, m, 5 × Ar-C*H*), 7.95 (2H, d, *J* = 6.0, 2 × Ar-C*H*), 7.88 – 7.58 (4H, m, 4 × Ar-C*H*), 7.50 (2H, d, *J* = 6.0, 2 × Ar-C*H*), 2.30 (3H,s, CH_3), 1.54 (3H, s, CH_3). Mass spec m/z ($C_{24}H_{19}N_3O_6$, MWt 445.43) 445 (7%), 399 (11%), 311 (23%), 150 (100%), 104 (33%), 77 (35%).

2.4. Synthesis of 1-(Acetophenone Oxime)-4-(*p*-Methylacetophenone Oxime) Diphenyl Carboxylate 5

An adapted literature procedure [8] was followed to synthesize the oxime ester **4**. In a round-bottomed flask, a solution of terphthaloyl chloride (2.03 g, 0.01 mmol) in chloroform (50 cm^3) was added dropwise to a solution of the acetophenone oxime **1** (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-methylacetophenone oxime **2** (0.149 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 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 **5** in a good yield (0.300 g, 0.725 mmol, 73 %) as an off-white solid. The product was recrystallized from diethyl ether. mp 195 – 200 ºC; IR ν_{max} (cm^{-1}) 1739 (2 × C=O, ester), 1604 (C=N), 1405 (C=N). ^{1}HNMR (DMSO-d6, 300 MHz) δ 7.95 – 7.90 (4 H, m, 4 × Ar-C*H*), 7.70 – 7.60 (4 H, m, 4 × Ar-C*H*), 7.59 – 7.40 (5 H, m, 5 × Ar-C*H*), 2.25 (3 H, s, CH_3), 1.85 (3 H, s, CH_3). Mass spec m/z ($C_{25}H_{22}N_2O_4$, MWt 414.46) 414 (80%), 337 (11%), 310 (15%), 281 (11%), 150 (100%), 118 (20%), 77 (80%).

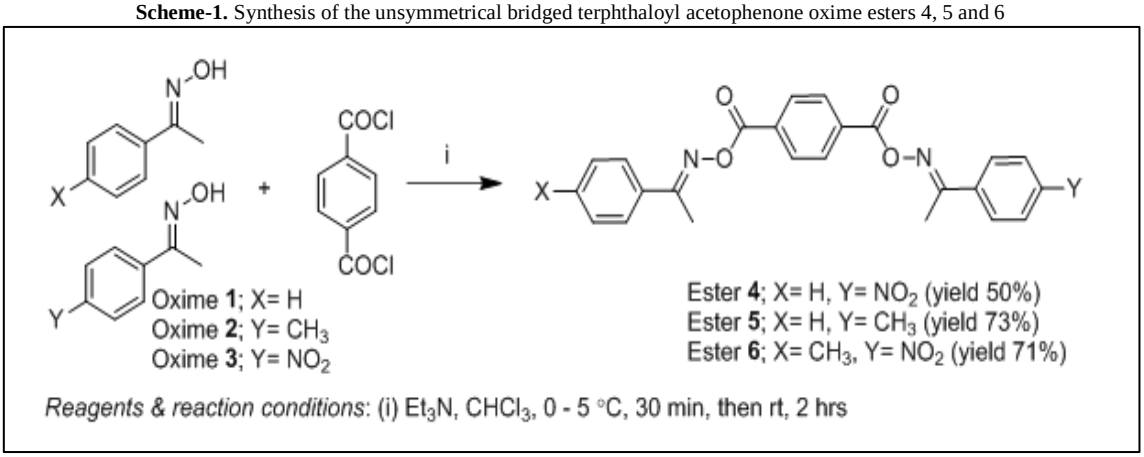
2.5. Synthesis of 1-(*p*-Methylacetophenone Oxime)-4-(*p*-Nitroacetophenone Oxime) Diphenyl Carboxylate 6

An adapted literature procedure [8] was followed towards the synthesis of the oxime ester **5**. 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-methylacetophenone oxime **2** (0.149 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-nitroacetophenone oxime **3** (0.180 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 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 in moderate yield (0.325g, 0.708 mmol, 71%) as an off-white solid. The product was recrystallized from diethyl ether. mp 212 °C; IR νmax (cm^{-1}) 1737 (2 × C=O, ester), 1602 (C=N), 1404 (C=N), 1376 (NO_2). ^{1}HNMR (DMSO-d6, 300 MHz) δ 7.95 (2H, d, *J* = 6.0, 2 × Ar-C*H*), 7.85 (2H, d, *J* = 6.0, 2 × Ar-C*H*), 7.63 (2H, d, *J* = 6.0, 2 × Ar-C*H*), 7.59 – 7.40 (4H, m, 4 × Ar-C*H*), 7.30 (2H, d, *J* = 6.0, 2 × Ar-C*H*), 2.29 (3H, s, CH_3), 2.27 (3H, s, CH_3), 1.31 (3H, s, CH_3). Mass spec m/z ($C_{25}H_{21}N_3O_6$, MWt 459.46) 459 (25%), 311 (21%), 280 (22%), 150 (100%), 132 (12%), 118 (13%), 91 (22%).

3. Results and Discussion

The acetophenone oxime **1** and 4-nitro acetophenone oxime **2** 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 ester **4** was obtained in moderate yield as an off-white solid. Similar approaches, altering the type of oxime accordingly, were followed towards obtaining oxime esters **5** and **6** as white solids (Scheme 1).

Scheme-1. Synthesis of the unsymmetrical bridged terphthaloyl acetophenone oxime esters 4, 5 and 6



The IR data revealed the disappearance of the oxime hydroxyl group and the formation of the two ester groups. The presence of the imino group (C=N) was indicated by the appearance of two rather weak sharp absorption bands. The ^{1}HNMR data of the oxime esters **4** – **6** revealed the formation of these oxime esters as all expected chemical shifts for all different protons were seen in the spectra and the disappearance of the hydroxyl proton of the starting oximes. The mass spectrometer gave a further evidence on the formation of all oxime esters **4** – **6**. The molecular ion peaks for all synthesized oxime esters **4** – **6** were observed at 445, 414 and 459 m/z along with other molecular fragments that were in a line with the expected theoretical fragmentation patterns.

4. Conclusion

Three unsymmetrical bridged terphthaloyl acetophenone oxime esters have been synthesized throughout an esterification step between three acetophenone oxime and the terphthaloyl chloride under mild basic conditions. The yields of the desired oxime esters were ranging from 50% to 73%.

Acknowledgments

Authors would like to thank Dr. Huda S. Elgobbi and Mr. Waleed A. Tanashi at the bioresearch office, Misurata University for their assistance throughout this research project.

References

[1] Jadhav, A., Gade, E., Angarkhe, B., and Durrani, A., 2018. "An efficient one pot synthesis of oxime by classical method." *International Journal of Chemical and Physical Sciences*, vol. 7, pp. 2319–6602.

[2] Vessally, E., Saeidian, H., Hosseinia, A., Edjlali, L., and Bekhradnia, A., 2017. "A review on synthetic applications of oxime esters." *Current Organic Chemistry*, vol. 21, pp. 249–271.

[3] Guo, J., Jin, T., Zhang, S., and Li, T., 2001. "An efficient and convenient catalyst for preparation of aromatic oximes." *Green Chemistry*, vol. 3, pp. 193–195.

[4] Bawa, R. A. and Friwan, M. M., 2019. "Synthesis and Antifungal Study of Some Acetophenone oximes and their terphthaloyl oxime esters." *Academic Journal of Chemistry*, vol. 5, pp. 96–101.

[5] Damljanovic´, I., Vuckovic´, M., and Rastko, D., 2006. "A simple synthesis of oximes." *Monatshefte fur Chemie*, vol. 137, pp. 301–305.

[6] Harikrishna, A., Kumar, K., and Elias, G., 2017. "Oxime esters as potential pharmacological agents– a review." *IJPCBS*, vol. 7, pp. 128–137.

[7] Komiyama, Y., Oishi, T., Ariyoshi, T., Tamachi, T., Ikaga, T., and Sato, N., 2019. "Oxime ester compound and photopolymerization initiator containing said compound." *U.S. Patent Application*, vol. 10, pp. 189–847.

[8] Bawa, R. A. and Friwan, M. M., 2019. "Synthesis of some acetophenone oximes and their corresponding bridged terphthaloyl oxime esters." *Academic Journal of Life Sciences*, vol. 5, pp. 87–92.