

Synthesis of Some Acetophenone Oximes and Their Corresponding Bridged Terphthaloyl Oxime Esters

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Abstract

The objective of this study is to synthesize a number of oximes along with their terphthaloyl oxime esters derived from acetophenone, 4-methylacetophenone, 4-hydroxyacetophenone, 4-aminoacetophenone and 4-nitroacetophenone as a part of ongoing research. Five acetophenone oximes have been synthesized by refluxing the acetophenone derivative with a solution of hydroxylamine hydrochloride in the presence of potassium hydroxide. The corresponding acetophenone oximes were obtained as solid materials in moderate to good yields. The structures of the resulting oximes were confirmed using IR, NMR and mass spectrometer. The HNMR data revealed that one oxime of the synthesized oximes was obtained as a mixture of two *E/Z* isomers in a ratio of (8:1). These resulting oximes were subjected into an esterification process with the terphthaloyl chloride in molar ratio of (1:2) respectively. The esterification reaction was carried out under basic conditions at 0 – 5 °C then room temperature. The five corresponding bridged terphthaloyl oxime esters have been formed as solid materials in moderate yields. The structures of the obtained terphthaloyl esters were also confirmed by spectroscopic techniques such as IR, NMR and mass spec.

Keywords: Oximes, acetophenone; Synthesized; Spectroscopic; *E/Z* isomers; Terphthaloyl; Esters.



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1. Introduction

Oximes are found in many bioactive molecules. These molecules have a wide range of activities, including antibacterial, antifungal, anti-inflammatory, antioxidant, anti-diabetes and cytotoxic activities as well as their use as precursors in the synthesis of photosensitive materials [1, 2]. The mono oxime, 4-(hydroxyimino) pentan-2-one, was synthesized through a solvent-free procedure yielding a *E/Z* isomeric mixture in a ratio of (9:1) according to the ¹HNMR data of crude product. The MM2 molecular mechanics method expectedly showed that the *E*-isomer of the (*E*)-4-(hydroxyimino) pentan-2-one was the favored as it has the lower total energy than the *Z*-isomer, (*Z*)-4-(hydroxyimino)pentan-2-one [1]. The corresponding benzoyl ester of the mono oxime, 4-(hydroxyimino)pentan-2-one, was also reported to be obtained in two isomeric conformations *Z/E* in a ratio of (9:1) according to the ¹HNMR data of crude product. However, the MM2 method unexpectedly predicted that the *Z*-isomer of the benzoyl ester has a lower energy than its counterpart *E*-isomer [1]. Oxime esters could be obtained by the reaction of keto- or aldoximes with acid chlorides or acid anhydrides. Oxime esters are important molecules for the synthesis of biologically active heterocyclic compounds [3]. Oxime esters have also been used to cleavage DNA [4-6], herbicidal and antitumor activities [7, 8]. Unsymmetrical dioxime esters such as (*2E,4E*)-(4-imino *O*-benzoyl-2-imino *O*-terphthaloyl)pentane, (*2E,4E*)-(4-imino *O*-benzoyl-2-imino *O*-tosyl)pentane and (*2E,4E*)-(4-imino *O*-terphthaloyl-2-imino *O*-tosyl)pentane have been synthesized and characterized [9].

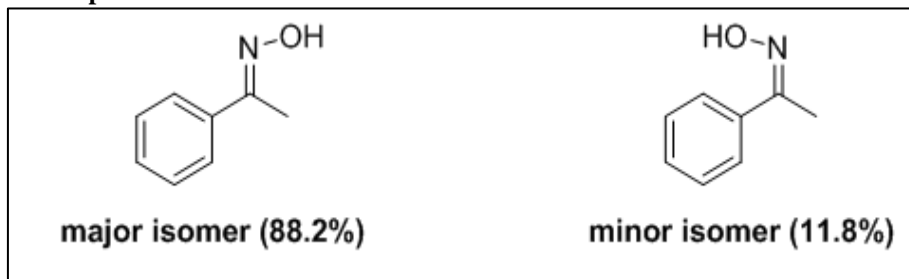
2. Materials and Methods

2.1. Materials

Acetophenone, 4-methylacetophenone, 4-hydroxyacetophenone, 4-aminoacetophenone, hydroxylamine hydrochloride, terphthaloyl chloride, potassium carbonate, anhydrous sodium sulphate, triethyl amine and chloroform. These chemicals were used without further purification.

2.2. Instrumentation

Melting points were measured on a Barnstead electrothermal IA 9100. ¹HNMR spectrum was recorded on a JEOL ECA-500 II spectrometer. Residual proton signal from the deuteriated solvent was used as reference [DMSO (¹H, 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 Shimadzu Qp-2010 Plus.

Synthesis of acetophenone oxime 1:

A literature procedure [1] was adapted towards the synthesis of the desired oxime. Solution of hydroxylamine hydrochloride (5.0 gm, 71.94 mmol in 10 cm³ of distilled water) and a solution of potassium hydroxide (3.0 gm, 53.48 mmol in 5 cm³ of distilled water) were placed in a round-bottomed flask and stirred at room temperature. Acetophenone (8.0 gm, 66.58 mmol) was then added while stirring and the reaction mixture was refluxed. At the start of boiling, small amounts of ethanol (5 cm³) were added from time to time to reaction mixture through the condenser until the boiling solution becomes clear. The reaction was left under reflux for further an hour after which the reaction vessel was allowed to cool gradually to room temperature. The pH of the reaction mixture was measured and found as expected to be acidic. A solution of 1N KOH was added to the reaction mixture until the solution became neutral. The reaction mixture was then refluxed for further 30 min, cooled to room temperature. The pH was measured and found to be still acidic. Addition of 1N KOH solution was required and the reaction mixture was refluxed for another 10 min, cooled, pH was measured and found to be neutral. The reaction mixture was transferred into a beaker containing ice – water (100 cm³), the acetophenone oxime was precipitated rapidly, filtered, washed with cold water (3 × 10 cm³) and air dried to give a white powder of the desired compound (2.80 gm, 20.74 mmol, 31% yield). The product was recrystallized from diethyl ether; mp 67 °C (lit. 55 – 60 °C, Aldrich); IR ν_{\max} (cm⁻¹) 3212 (OH), 1497 (C=N). **Major isomer (88.2 %):** ¹HNMR (DMSO-d₆, 500 MHz) δ 11.24 (1 H, s, OH), 7.65 (2 H, d, *J* 7.7, 2 × Ar-CH), 7.38 – 7.32 (3 H, m, 3 × Ar-CH), 2.15 (3 H, s, CH₃); **Minor isomer (11.8%):** ¹HNMR (DMSO-d₆, 500 MHz) δ 11.23 (1 H, s, OH), 7.94 (2 H, d, *J* 7.9, 2 × Ar-CH), 7.52 – 7.49 (3 H, m, 3 × Ar-CH), 2.56 (3 H, s, CH₃). Mass spec *m/z* (C₈H₉NO, MWt 135.15) 135 (75%), 118 (22%), 106 (40%), 94 (42%), 77 (100%).

Synthesis 4-methyl acetophenone oxime 2:

A literature procedure [1] was adapted towards the synthesis of the desired oxime. Solution of hydroxylamine hydrochloride (5.0 gm, 71.94 mmol in 10 cm³ of distilled water) and a solution of potassium hydroxide (3.0 gm, 53.48 mmol in 5 cm³ of distilled water) were placed in a round-bottomed flask and stirred at room temperature. 4-Methyl acetophenone (8.0 gm, 59.62 mmol) was then added while stirring and the reaction mixture was refluxed. At the start of boiling, small amounts of ethanol (5 cm³) were added from time to time to reaction mixture through the condenser until the boiling solution becomes clear. The reaction was left under reflux for further an hour after which the reaction vessel was allowed to cool gradually to room temperature. The pH of the reaction mixture was measured and found as expected to be acidic. A solution of 1N KOH was added to the reaction mixture until the solution became neutral. The reaction mixture was then refluxed for further 30 min, cooled to room temperature. The pH was measured and found to be still acidic. Addition of 1N KOH solution was required and the reaction mixture was refluxed for another 10 min, cooled, pH was measured and found to be neutral. The reaction mixture was transferred into a beaker containing ice – water (100 cm³), the 4-methyl acetophenone oxime was precipitated rapidly, filtered, washed with cold water (3 × 10 cm³) and air dried to give a white powder of the desired compound (4.50 gm, 30.16 mmol, 51% yield). The product was recrystallized from diethyl ether; mp 93 °C; IR ν_{\max} (cm⁻¹) 3212 (OH), 1513 (C=N). ¹HNMR (DMSO-d₆, 500 MHz) δ 11.08 (1 H, s, OH), 7.52 (2 H, d, *J* 7.5, 2 × Ar-CH), 7.17 (2 H, d, *J* 7.2, 2 × Ar-CH), 2.29 (3 H, s, CH₃), 2.11 (3 H, s, CH₃). Mass spec *m/z* (C₉H₁₁NO, MWt 149.19) 149 (90%), 132 (20%), 117 (23%), 107 (22%), 94 (100%), 65 (53%).

Synthesis of 4-hydroxy acetophenone oxime 3:

A literature procedure [1] was adapted towards the synthesis of the desired oxime. Solution of hydroxylamine hydrochloride (5.0 gm, 71.94 mmol in 10 cm³ of distilled water) and a solution of potassium hydroxide (3.0 gm, 53.48 mmol in 5 cm³ of distilled water) were placed in a round-bottomed flask and stirred at room temperature. 4-Hydroxy acetophenone (8.0 gm, 58.76 mmol) was then added while stirring and the reaction mixture was refluxed. At the start of boiling, small amounts of ethanol (5 cm³) were added from time to time to reaction mixture through the condenser until the boiling solution becomes clear. The reaction was left under reflux for further an hour after which the reaction vessel was allowed to cool gradually to room temperature. The pH of the reaction mixture was measured and found as expected to be acidic. A solution of 1N KOH was added to the reaction mixture until the solution became neutral. The reaction mixture was then refluxed for further 30 min, cooled to room temperature. The pH was measured and found to be still acidic. Addition of 1N KOH solution was required and the reaction mixture was refluxed for another 10 min, cooled, pH was measured and found to be neutral. The reaction mixture was transferred into a beaker containing ice – water (100 cm³), the 4-hydroxy acetophenone oxime was precipitated rapidly, filtered, washed with cold water (3 × 10 cm³) and air dried to give a white powder of the desired compound (4.10 gm, 27.12 mmol, 46% yield). The product was recrystallized from diethyl ether; mp 140 °C (lit. 142 – 144 °C, Aldrich); IR ν_{\max} (cm⁻¹) 3267 (2 × OH), 1640 (C=N). ¹HNMR (DMSO-d₆, 500 MHz) δ 10.86 (1 H, s, OH, oxime), 9.67 (1 H, s, OH, phenolic), 7.45 (2 H, d, *J* 7.5, 2 × Ar-CH), 6.75 (2 H, d, *J* 6.8, 2 × Ar-CH), 2.07 (3 H, s, CH₃). Mass spec *m/z* (C₈H₉NO₂, MWt 151.16) 151 (100%), 134 (40%), 119 (30%), 110 (15%), 94 (60%), 65 (80%).

Synthesis 4-amino acetophenone oxime 4:

A literature procedure [1] was adapted towards the synthesis of the desired oxime. Solution of hydroxylamine hydrochloride (5.0 gm, 71.94 mmol in 10 cm³ of distilled water) and a solution of potassium hydroxide (3.0 gm, 53.48 mmol in 5 cm³ of distilled water) were placed in a round-bottomed flask and stirred at room temperature. 4-Amino acetophenone (8.0 gm, 59.19 mmol) was then added while stirring and the reaction mixture was refluxed. At the start of boiling, small amounts of ethanol (5 cm³) were added from time to time to reaction mixture through the condenser until the boiling solution becomes clear. The reaction was left under reflux for further an hour after which the reaction vessel was allowed to cool gradually to room temperature. The pH of the reaction mixture was measured and found as expected to be acidic. A solution of 1N KOH was added to the reaction mixture until the solution became neutral. The reaction mixture was then refluxed for further 30 min, cooled to room temperature. The pH was measured and found to be still acidic. Addition of KOH solution 1 N was required and the reaction mixture was refluxed for another 10 min, cooled, pH was measured and found to be neutral. The reaction mixture was transferred into a beaker containing ice – water (100 cm³), the 4-amino acetophenone oxime was precipitated rapidly, filtered, washed with cold water (3 × 10 cm³) and air dried to give a deep brown solid of the desired compound (5.0 gm, 33.29 mmol, 56% yield). The product was recrystallized from diethyl ether; mp 150 °C (lit. 153 °C, chemical book website); IR ν_{\max} (cm⁻¹) 3352 (OH), 3289 and 3162 (NH₂), 1632 (C=N). ¹HNMR (DMSO-d₆, 500 MHz) δ 7.32 (2 H, d, *J* 7.3, 2 × Ar-CH), 6.53 (2 H, d, *J* 6.5, 2 × Ar-CH), 5.32 (2 H, br s, NH₂), 2.02 (3 H, s, CH₃). Mass spec *m/z* (C₈H₁₀N₂O, MWt 150.18) 150 (100%), 133 (50%), 118 (35%), 93 (40%), 65 (60%).

Synthesis 4-nitro acetophenone oxime 5:

A literature procedure [1] was adapted towards the synthesis of the desired oxime. Solution of hydroxylamine hydrochloride (5.0 gm, 71.94 mmol in 10 cm³ of distilled water) and a solution of potassium hydroxide (3.0 gm, 53.48 mmol in 5 cm³ of distilled water) were placed in a round-bottomed flask and stirred at room temperature. 4-Nitro acetophenone (8.0 gm, 48.44 mmol) was then added while stirring and the reaction mixture was refluxed. At the start of boiling, small amounts of ethanol (5 cm³) were added from time to time to reaction mixture through the condenser until the boiling solution becomes clear. The reaction was left under reflux for further an hour after which the reaction vessel was allowed to cool gradually to room temperature. The pH of the reaction mixture was measured and found as expected to be acidic. A solution of 1N KOH was added to the reaction mixture until the solution became neutral. The reaction mixture was then refluxed for further 30 min, cooled to room temperature. The pH was measured and found to be still acidic. Addition of KOH solution 1N was required and the reaction mixture was refluxed for another 10 min, cooled, pH was measured and found to be neutral. The reaction mixture was transferred into a beaker containing ice – water (100 cm³), the 4-nitro acetophenone oxime was precipitated rapidly, filtered, washed with cold water (3 × 10 cm³) and air dried to give a yellow solid of the desired compound (7.20 gm, 39.97 mmol, 83% yield). The product was recrystallized from diethyl ether; mp 172 °C (lit. 169 – 171 °C) [10]; IR ν_{\max} (cm⁻¹) 3220 (OH), 1601 (C=N), 1511 and 1337 (NO₂). ¹HNMR (DMSO-d₆, 500 MHz) δ 11.79 (1 H, s, OH), 8.22 (2 H, d, *J* 8.21, 2 × Ar-CH), 7.90 (2 H, d, *J* 7.89, 2 × Ar-CH), 2.19 (3 H, s, CH₃). Mass spec *m/z* (C₈H₈N₂O₃, MWt 180.16) 180 (100%), 163 (20%), 133 (22%), 117 (40%), 102 (23%), 89 (38%), 76 (60%), 65 (40%).

Synthesis of 1-phenylethan-1-one O-[4-(1-phenylethylideneamino) oxycarbonyl benzoyl oxime 6:

An adapted literature procedure [1] was followed to synthesis title compound. The acetophenone oxime (2.97 g, 0.022 mmol) in chloroform (40 cm³) in the presence of triethyl amine (0.66 g, 1.30 mmol) were placed in a round-bottomed flask and stirred at 0 – 5 °C. A solution of terphthaloyl chloride (2.03 g, 0.01 mmol) in chloroform (50 cm³) was then added dropwise over 30 min. The reaction mixture was left stirring at room temperature for 2 hours, after which distilled water (30 cm³) was added to the mixture and stirred for further 10 min. The organic layer was extracted, dried over anhydrous Na₂SO₄ and filtered. The solvent was evaporated *in vacuo* to obtain the desired oxime ester in moderate yield (4.03 g, 10.08 mmol, 46%) as off white solid. The product was recrystallized from diethyl ether. mp 183 °C; IR ν_{\max} (cm⁻¹) 1710 (C=O, ester), 1683 (C=O, ester), 1429 (C=N) and 1408 (C=N). ¹HNMR (DMSO-d₆, 400 MHz) δ 8.22 – 8.17 (2H, m, 2 × Ar-CH), 8.15 – 8.11 (2H, m, 2 × Ar-CH), 8.10 – 8.03 (8H, m, 8 × Ar-CH), 7.85 – 8.83 (1H, m, Ar-CH), 7.55 – 7.50 (1H, m, Ar-CH), 1.33 (6H, s, 2 × CH₃).

Synthesis of *o,o'*-terephthaloyl bis-1-(*p*-tolyl)-1-(*p*-tolyl)ethan-1-one oxime 7:

An adapted literature procedure [1] was followed to synthesis title compound. The 4-methyl acetophenone oxime (3.27 g, 0.022 mmol) in chloroform (40 cm³) in the presence of triethyl amine (0.66 g, 1.3 mmol) were placed in a round-bottomed flask and stirred at 0 – 5 °C. A solution of terphthaloyl chloride (2.03 g, 0.01 mmol) in chloroform (50 cm³) was then added dropwise over 30 min. The reaction mixture was left stirring at room temperature for 2 hours, after which distilled water (30 cm³) was added to the mixture and stirred for further 10 min. The organic layer was extracted, dried over anhydrous Na₂SO₄ and filtered. The solvent was evaporated *in vacuo* to obtain the desired oxime ester in moderate yield (3.20 g, 7.48 mmol, 34%) as pale brown solid. The product was recrystallized from diethyl ether. mp 186 °C; IR ν_{\max} (cm⁻¹) 1735 (C=O, ester), 1678 (C=O, ester), 1605 (C=N), 1574 (C=N). ¹HNMR (DMSO-d₆, 400 MHz) δ 7.89 (2H, d, *J* 7.9, 2 × Ar-CH), 7.82 (4H, d, *J* 7.8, 4 × Ar-CH), 7.70 (4H, d, *J* 7.7, 4 × Ar-CH), 7.57 (2H, d, *J* 7.6, 2 × Ar-CH), 2.51 (6H, s, 2 × Ar-CH₃), 2.34 (6H, s, 2 × CH₃). Mass spec *m/z* (C₂₆H₂₄N₂O₄, MWt 428.17) 428 (40%), 386 (99%), 344 (20%), 280 (95%), 255 (18%), 149 (100%), 91 (60%), 65 (70%).

Synthesis of *o,o'*-terephthaloyl bis-1-(4-hydroxyphenyl)-1-(4-hydroxyphenyl) ethan-1-one oxime 8:

An adapted literature procedure [1] was followed to synthesis title compound. The 4-hydroxy acetophenone oxime (3.32 g, 0.022 mmol) in chloroform (40 cm³) in the presence of triethyl amine (0.66 g, 1.30 mmol) were placed in a round-bottomed flask and stirred at 0 – 5 °C. A solution of terphthaloyl chloride (2.030 g, 0.010 mmol) in chloroform (50 cm³) was then added dropwise over 30 min. The reaction mixture was left stirring at room

temperature for 2 hours, after which distilled water (30 cm³) was added to the mixture and stirred for further 10 min. The organic layer was extracted, dried over anhydrous Na₂SO₄ and filtered. The solvent was evaporated *in vacuo* to obtain the desired oxime ester in moderate yield (3.20 g, 7.41 mmol, 32%) as white solid. The product was recrystallized from diethyl ether. mp 147 °C; IR ν_{\max} (cm⁻¹) 3410 (2 × OH, ester), 1730 (2 × C=O, ester), 1596 (2 × C=N). ¹HNMR (DMSO-d₆, 400 MHz) δ 8.23 (2H, s, 2 × Ar-OH), 8.16 (1H, d, *J* 8.2, Ar-CH), 8.10 (1H, d, *J* 8.1, Ar-CH), 7.81 (2H, d, *J* 7.8, 2 × Ar-CH), 7.45 (2H, d, *J* 7.5, 2 × Ar-CH), 7.26 – 7.06 (2H, m, 2 × Ar-CH), 6.84 (2H, d, *J* 6.8, 2 × Ar-CH), 6.75 (2H, d, *J* 6.8, 2 × Ar-CH), 2.46 (6H, s, 2 × CH₃). Mass spec *m/z* (C₂₄H₂₀N₂O₆, MWt 432.13) 432 (15%), 417 (5%), 390 (12%), 348 (15%), 299 (22%), 257 (100%), 149 (50%), 109 (40%), 65 (40%).

Synthesis of *o,o'*-terephthaloyl bis-1-(4-aminophenyl)-1-(4-aminophenyl) ethan-1-one oxime 9:

An adapted literature procedure [1] was followed to synthesis title compound. The 4-amino acetophenone oxime (3.30 g, 0.022 mmol) in chloroform (40 cm³) in the presence of triethyl amine (0.66 g, 1.30 mmol) were placed in a round-bottomed flask and stirred at 0 – 5 °C. A solution of terphthaloyl chloride (2.03 g, 0.010 mmol) in chloroform (50 cm³) was then added dropwise over 30 min. The reaction mixture was left stirring at room temperature for 2 hours, after which distilled water (30 cm³) was added to the mixture and stirred for further 10 min. The organic layer was extracted, dried over anhydrous Na₂SO₄ and filtered. The solvent was evaporated *in vacuo* to obtain the desired oxime ester in moderate yield (5.40 g, 12.09 mmol, 57%) as deep green solid. The product was recrystallized from diethyl ether. mp 185 °C; IR ν_{\max} (cm⁻¹) 3358 (2 × NH₂, ester), 1743 (2 × C=O, ester), 1651 (2 × C=N). ¹HNMR (DMSO-d₆, 400 MHz) δ 7.65 (2H, d, *J* 7.7, 2 × Ar-CH), 7.48 (4H, d, *J* 7.5, 4 × Ar-CH), 7.25 (2H, d, *J* 7.3, 2 × Ar-CH), 6.86 (4H, d, *J* 6.9, 4 × Ar-CH), 3.41 (4H, br s, 2 × NH₂), 2.07 (6H, s, 2 × CH₃). Mass spec *m/z* (C₂₄H₂₂N₄O₄, MWt 430.16) 430 (8%), 397 (20%), 324 (20%), 298 (60%), 256 (20%), 192 (20%), 175 (22%), 149 (60%), 108 (100%), 65 (98%).

Synthesis of *o,o'*-terephthaloyl bis-1-(4-nitrophenyl)-1-(4-nitrophenyl) ethan-1-one oxime 10:

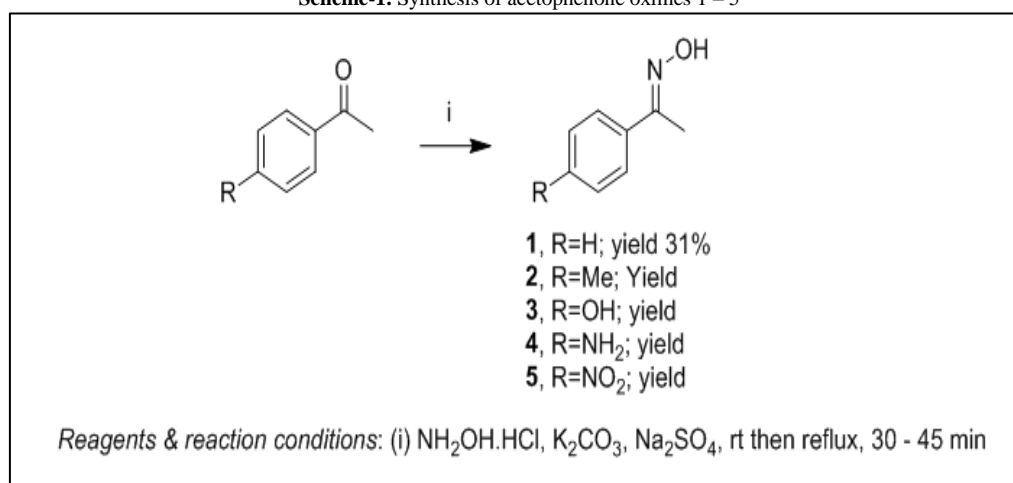
An adapted literature procedure [1] was followed to synthesis title compound. The 4-nitro acetophenone oxime (3.96 g, 0.022 mmol) in chloroform (40 cm³) in the presence of triethyl amine (0.66 g, 1.30 mmol) were placed in a round-bottomed flask and stirred at 0 – 5 °C. A solution of terphthaloyl chloride (2.03 g, 0.01 mmol) in chloroform (50 cm³) was then added dropwise over 30 min. The reaction mixture was left stirring at room temperature for 2 hours, after which distilled water (30 cm³) was added to the mixture and stirred for further 10 min. The organic layer was extracted, dried over anhydrous Na₂SO₄ and filtered. The solvent was evaporated *in vacuo* to obtain the desired oxime ester in moderate yield (4.0 g, 8.16 mmol, 37%) as yellow solid. The product was recrystallized from diethyl ether. mp 177 °C; IR ν_{\max} (cm⁻¹) 1742 (2 × C=O, ester), 1600 (2 × C=N), 1523 (2 × NO₂, ester), 1347 (2 × NO₂, ester). ¹HNMR (DMSO-d₆, 400 MHz) δ 8.35 – 8.31 (2H, m, 2 × Ar-CH), 8.21 (4H, d, *J* 8.2, 4 × Ar-CH), 8.13 – 8.09 (2H, m, 2 × Ar-CH), 7.90 (4H, d, *J* 7.9, 4 × Ar-CH), 2.20 (6H, s, 2 × CH₃). Mass spec *m/z* (C₂₄H₁₈N₄O₈, MWt 490.11) 490 (40), 467 (35), 453 (38), 425 (39), 394 (38), 368 (95), 353 (43), 163 (39), 149 (54), 103 (45), 83 (100), 65 (50).

3. Results and Discussion

3.1. Synthesis of Acetophenone Oximes 1 – 5

The acetophenone derivative was refluxed with a solution of hydroxylamine hydrochloride in the presence of potassium hydroxide. The corresponding acetophenone oximes were formed as solid materials in moderate to good yields (Scheme 1).

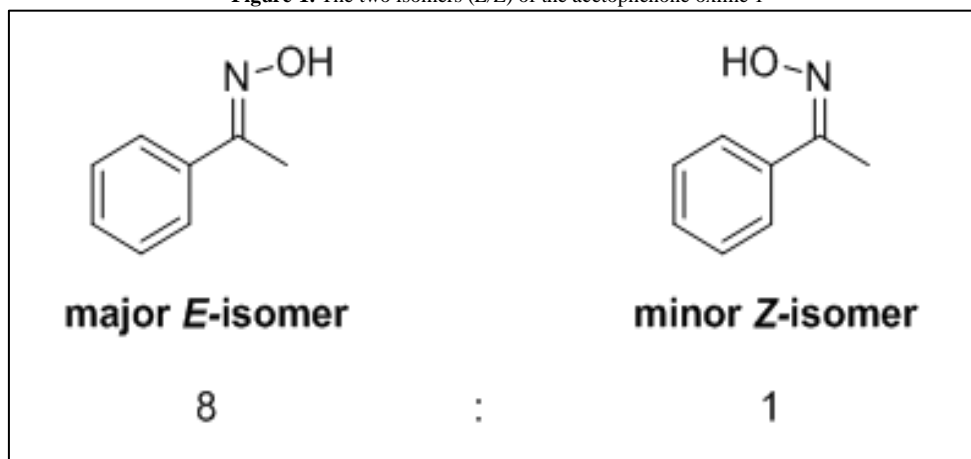
Scheme-1. Synthesis of acetophenone oximes 1 – 5



The spectroscopic analysis for the resulting compounds revealed the formation of the acetophenone oximes 1 – 5. The IR data showed the absorption of the hydroxyl group and the imino group (C=N) at the expense of the carbonyl group (C=O) of the acetophenone derivative. The mass spectrometer gave the expected molecular masses along with the fragmentation patterns for all acetophenone oximes 1 – 5. The ¹HNMR further confirmed the formation of all oximes 1 – 5. The ¹HNMR spectroscopic data showed that the acetophenone oximes 2 – 5 were

obtained as single isomers except the acetophenone oxime **1**, which was obtained in two isomeric forms *E/Z* in ratio of about (8:1) (**Fig 1**) [Mona's 3rd conference paper].

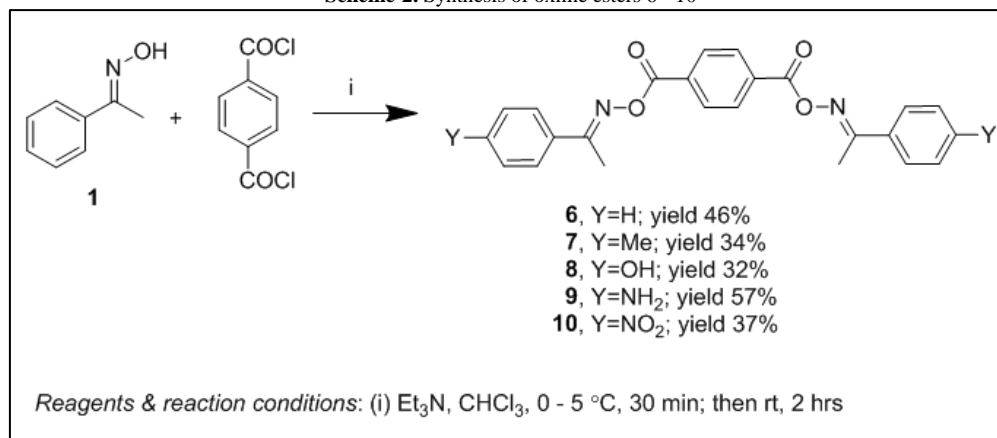
Figure-1. The two isomers (*E/Z*) of the acetophenone oxime **1**



Synthesis of the bridged terphthaloyl acetophenone oxime esters **6 – 10**:

An adapted literature procedure [1] was followed towards the synthesis of the oxime esters **6 – 10**. The acetophenone oxime derivative was reacted with terphthaloyl chloride in the ratio of (2:1 mole/mole) under mild basic conditions at 0 °C to room temperature. The desired terphthaloyl oxime esters **6 – 10** were obtained in moderate yields as solid materials (**Scheme 2**).

Scheme-2. Synthesis of oxime esters **6 - 10**



The IR data revealed the disappearance of the oxime hydroxyl group and the formation of the ester groups (COO) as strong absorption bands for all oxime esters **6 – 10**. The ¹HNMR data of the oxime ester **6** revealed the formation of this ester as all expected chemical shifts for all different protons were seen in the spectrum and the disappearance of the oxime hydroxyl proton of the starting oximes. The mass spectrometer gave a further evidence on the formation of the oxime ester **6**. The molecular ion peak was observed at 400, 428, 432, 430 and 490 m/z along with other molecular fragments for the oxime esters **6 – 10** respectively, which were in a line with the expected theoretical fragmentation patterns.

4. Conclusion

Five oximes derived from the acetophenone have been synthesized in moderate to good yields. Only the acetophenone oxime was obtained in two *E/Z* isomeric forms in a ratio of (8:1). These five resulting oximes were subjected into an esterification reaction with the terphthaloyl chloride in molar ratio of (1:2) through which five bridged terphthaloyl oxime esters have been formed in moderate yields.

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