Synthesis of Six and Seven-membered Heterocyclic Molecules Containing an Adamantyl Fragment and an X-ray Crystal Structure of (E)-N-(adamantan-1-yl)-1-(3-nitrophenyl)methanimine

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Abstract:
Our work included a synthesis of three new imine derivatives—1,3-thiazinan-4-one, 1,3-oxazinan-6-one and 1,3-oxazepin-4,7-dione—which contained an adamantyl fragment. These were produced via the condensation of the Schiff’s base (E)-N-(adamantan-1-yl)-1-(3-aryl)methanimine with 3-mercaptopropanoic acid; 3-chloropropanoic acid; and maleic, citraconic anhydride, respectively. These new imines were prepared via the condensation of adamantan-1-ylamine and 3-nitro-, 3-bromobenzaldehyde in n-BuOH. We obtained a good yield of products. FTIR, 1H NMR spectroscopy and C.H.N.S analysis were used to diagnostic the products. The molecular structure of (E)-N-(adamantan-1-yl)-1-(3-nitrophenyl)methanimine was confirmed by X-ray crystallography analysis.

Keywords: Adamantan-1-ylamine, 1,3-oxazepin-4,7-dione, 1,3-oxazinan-6-one, 1,3-thiazinan-4-one, X-ray crystallography.

Introduction:
The molecular skeleton of adamantane and its derivatives molecules are of current interest to researchers in molecular technology. Adamantan-1-ylamine and its derivatives are amines containing adamantyl fragment in the form of three fused cyclohexane rings in a chair conformation (1), and adamantane is the monomer of the diamond lattice (2). The adamantyl group has been found to be an important component in the development of many drug treatments (3). For example, the addition of adamantyl moiety to an active pharmaceutical molecule leads to improvements in an array of therapeutic drugs (4), and adamantan-1-ylamine was the first anti-viral treatment to be developed (5). This development led to the synthesis and testing of hundreds of adamantylamine derivatives for different bioactivities, especially for cancer drugs. The synthesis and study of the bioactivity of (E)-N-(adamantan-1-yl)-1-(3-aryl) methanimine derivatives have been undertaken via the condensation of two components of adamantan-1-ylamine together with various aromatic aldehydes in the presence of acetic acid, and some of the synthesized compounds have been reported to inhibit acetylcholinesterase (ACHE) and to have anti-microbial, anti-cancer impacts in vitro and anti-inflammatory (6-11).

Furthermore, azomethine (imine) compounds are reactive intermediaries for organic synthesis in a number of diverse fields (12,13).

Thiazine, oxazine and oxazepine have similar structures for six and seven-membered heterocyclic compounds which contain two hetero atoms (S, N) and (O, N), respectively (14-16). Oxazepinone is synthesized via a cyclo-addition reaction (2+5) between imine and anhydride (17-20). Whereas, thiazinanone prepared via the condensation of pyridin-2-ylmethanimine, benzaldehyde derivatives, and 3-mercaptopropanoic acid (14,20). The reaction between imine and glycolic acid gave oxazinone (21). These three classes of compounds have very great interest in medical treatments such as anti-bacterial, anti-viral and anti-oxidant properties (22-25). Adamantan-1-ylamine derivatives gave a potential value for the development of beneficial bioactivities drugs. This research presents promising synthesis ofadamantanylarnethaniminines as predecessors of six and seven-membered heterocyclic molecules containing an adamantyl fragment. The single-crystal structure of (E)-N-(adamantan-1-yl)-1-(3-
nitrophénylméthanamine was affirmed by X-ray crystallography analysis.

Materials and Methods:
All materials and solvents were supplied by Sigma-Aldrich Chemical Co. (Germany) and Romil Co. (UK). Melting point temperatures were measured using the Stuart SMP-10 apparatus. FTIR and ¹H NMR spectra were recorded using the Bruker-Tensor 27 and Bruker-300 MHz spectrometers, respectively (with DMSO-d₆ and CDCl₃ as a solvents and TMS as internal standard). Microelemental analysis was performed by using a thermo scientific flash 2000 series analyser, whilst X-ray diffraction was measured using a STOE StadiVari Pilatus100K diffractometer. The progress of reactions were monitored by TLC Silica gel 60G F254 (Sigma-Aldrich) using eluent chloroform/acetone (6:1) and benzene/methanol (7:1) as mobile phase under iodine vapour.

The general procedure for synthesizing (E)-N-(adamantan-1-yl)-1-(3-arylimino)methanimine (1a, b)
1a was synthesized using a simple procedure with comparing (6)
A solution of 0.013 mol adamantan-1-ylamine in 20 mL butanol was added to a 0.013 mol solution of suitable 3-substituted benzaldehyde in 15 mL butanol. The mixture was heated for 1-1.5 hours with stirring at the boiling point of the solvent. The solvent was evaporated, and the residual product was re-crystallized from i-PrOH.

Description of the properties of (1a and 1b)
(E)-N-(adamantan-1-yl)-1-(3-nitrophénylméthanamine (1a)
The reaction of adamantan-1-ylamine (1.96 g, 0.013 mol) and 3-nitrobenzaldehyde (1.96 g, 0.013 mol) gave (1a) as a white crystals, yield 3.4 g, 91%; mp 117–118° C. Found C₁₇H₂₀N₂O₂ (%): C 71.17, H 7.68, N 9.50. Calculated (%): C 71.81, H 7.09, N 9.85. ¹H NMR (300 MHz, DMSO-d₆), δ, ppm: 8.58 (1H, s, CH=N); phenyl group (H₅, H₆, H₇, aromatic): 8.47 (1H, d, J=9 Hz, H₅), 8.17 (1H, d, J=9 Hz, H₆), 7.74 (1H, t, J=9 Hz, H₇); adamantyl group: 2.13 (3H, s, 3CH), 1.64-1.78 (12H, m, 6CH₂). FTIR (ν cm⁻¹): 3092 (C-H( aromatic)), 2903, 2848 (C-H( aliphatic)). 1638 (C≡N), 1522, 1343 (C=O). Details of the physical properties, C.H.N.S analysis, data of FTIR and ¹H NMR spectroscopy were determined for products (1a, b-5a, b) and (1a, b-4a, b), respectively, and are displayed in Tables 1-4. X-ray analysis of compound (1a): Single crystal was obtained by allowing i-PrOH solution of the compound to stand for one week. The crystallographic data is shown in Tables 5-7.

Table 1. Physical properties and C.H.N.S analysis of the compounds (1a, b-5a, b).

| Comp.№ | M. Formula | Color | Solvent of re-cryst. | Yield% | mp °C | C.H.N.S analysis |
|---------|------------|-------|---------------------|--------|-------|------------------|
|         |            |       |                     |        |       | Found (%) / Calculated (%) |
|         |            |       |                     |        |       | C H N S          |
| 1a      | C₁₇H₂₀N₂O₂ | White crystals | 2-Propanol | 91    | 117-118 | 71.17 / 71.81, 7.68 / 7.09, 9.50 / 9.85 |
| 1b      | C₁₇H₂₀BrN  | White crystals | 2-Propanol  | 94    | 101-102 | 63.85 / 64.16, 6.10 / 6.33, 3.92 / 4.40 |
| 2a      | C₁₂H₁₀N₂O₃ | White powder | 1,4-Dioxane | 65    | 250-251 | 65.58 / 65.96, 6.10 / 5.80, 6.92 / 7.33 |
| 2b      | C₁₂H₁₂BrNO₃ | White powder | 1,4-Dioxane | 69    | 239-240 | 60.09 / 60.59, 4.95 / 5.33, 3.70 / 3.36 |
| 3a      | C₁₂H₁₀N₂O₃ | White powder | 1,4-Dioxane | 77    | 218-219 | 67.10 / 66.65, 5.31 / 6.10, 6.52 / 7.07 |
| 3b      | C₁₂H₁₂BrNO₃ | White powder | 1,4-Dioxane | 74    | 176-177 | 62.10 / 61.40, 5.15 / 5.62, 3.78 / 3.25 |
| 4a      | C₁₀H₁₀N₂O₂ | White powder | Ethanol    | 57    | 188-189 | 66.80 / 67.40, 7.23 / 6.79, 8.30 / 7.86 |
| 4b      | C₁₀H₁₂BrNO₂ | White powder | Ethanol    | 61    | 174-175 | 61.95 / 61.54, 6.93 / 6.20, 3.15 / 3.59 |
| 5a      | C₁₀H₁₂N₂O₃S | White powder | Ethanol    | 64    | 290 decomp. | 65.15 / 60.05, 6.93 / 6.44, 6.85 / 7.52, 7.84 / 8.61 |
| 5b      | C₁₀H₁₂BrNOS | White powder | Ethanol    | 68    | 280 decomp. | 59.11 / 60.54, 5.95 / 6.44, 3.45 / 3.82, 7.89 / 8.54 |
(E)-N-(adamantan-1-yl)-1-(3-bromophenyl)methanimine (1b)

The reaction of adamantant-1-ylamine (1.96 g, 0.013 mol) and 3-bromobenzaldehyde (2.4 g, 0.013 mol) gave (1b) as a white crystals, yield 3.38 g, 94%; mp 101–102°C. Found C_{21}H_{32}BrN (%): C 63.85, H 6.10, N 3.92. Calculated (%): C 64.16, H 6.33, N 4.40. ^1H NMR (300 MHz, DMSO-d6), δ, ppm: 8.29 (1H, s, CH=N); phenyl group (H$_a$, H$_b$, H$_g$ aromatic): 7.94 (1H, s, H$_d$), 7.73 (1H, d, J=6 Hz, H$_e$), 7.61 (1H, d, J=6 Hz, H$_b$), 7.40 (1H, t, J=9 Hz, H$_f$); adamantyl group: 2.12 (3H, s, 3CH$_3$), 1.63-1.74, 1.40 (12H, m, 6CH$_2$). FTIR (ν cm$^{-1}$): 3052 (C-H aromatic), 2906, 2811 (C-H aliphatic), 1631 (C=N), 776 (C-Br).

Table 2. FTIR and $^1$H NMR spectral data for compounds (1a,b).

| Comp. | ν C-H aromatic (ν cm$^{-1}$) | ν C-H aliphatic (ν cm$^{-1}$) | ν C≡N (ν cm$^{-1}$) | -NO$_2$ (ν cm$^{-1}$) | C-Br (ν cm$^{-1}$) | $^1$H NMR chemical shift (DMSO-d$_6$, δ, ppm) |
|-------|----------------------------|----------------------------|----------------|----------------|----------------|---------------------------------|
| 1a    | 1617, s, 1605, s, 1581, s | 2903, 2848                 | 1522, 1343      | -              | 8.58 (s)       | 8.47 (1H, s, H$_2$), 8.27 (1H, d, J=9 Hz, H$_3$), 8.17 (1H, d, J=9 Hz, H$_4$), 7.74 (1H, t, J=9 Hz, H$_5$), 1.78 (12H, m, 6CH$_2$) |
| 1b    | 1617, s, 1605, s, 1581, s | 2906, 2811                 | 1631, -          | -              | 8.29 (s)       | 7.94 (1H, s, H$_2$), 7.73 (1H, t, J=6 Hz, H$_3$), 7.61 (1H, d, J=6 Hz, H$_4$), 7.40 (1H, t, J=9 Hz, H$_5$), 1.40 (12H, m, 6CH$_2$) |

Table 2. FTIR and $^1$H NMR spectral data for compounds (1a,b).

The general procedure for synthesizing 3-(adamantan-1-yl)-2-(3-ary)-2,3-dihydro-1,3-oxazepin-4,7-dione and 3-(adamantan-1-yl)-6-methyl-2-(3-ary)-2,3-dihydro-1,3-oxazepin-4,7-dione (2a,b), (3a,b)

To a hot solution of 0.01 mol compounds 1a,b in 15 mL dry benzene was added to convenient solution of 0.01 mol anhydrides (maleic, citraconic) in 10 mL dry benzene. The mixture was refluxed for 7-10 hours with strong stirring, then the solvent was vaporized. The residual solid was washed with solution 3% NaHCO$_3$ and then three times with water. The product was dried and re-crystallized twice from 1,4-dioxane.

Description of the properties of (2a,b and 3a,b)

3-(adamantan-1-yl)-2-(3-nitrophenyl)-2,3-dihydro-1,3-oxazepin-4,7-dione (2a)

The reaction of imine (1a) (2.84 g, 0.01 mol) and maleic anhydride (0.98 g, 0.01 mol) gave (2a) as a white powder, yield 2.8 g, 69%; mp 239–240°C. Found C$_{21}$H$_{25}$N$_2$O$_5$ (%): C 62.69, H 5.40, N 3.70. Calculated (%): C 62.59, H 5.33, N 3.06. $^1$H NMR (300 MHz, DMSO-d$_6$), δ, ppm: 8.21 (1H, s, H$_2$), 7.87-8.11 (1H, m, H$_3$), 7.50-7.65 (1H, m, H$_4$), 7.43-7.60 (1H, m, H$_5$), 6.11 (1H, dd, J=6Hz, H$_4$), 9Hz, =C-CH-CO-N), 4.12 (1H, dd, J=6Hz, 6Hz, =C-CH-CO-O), adamantyl group: 1.63-1.76 (12H, m, 6CH$_2$). FTIR (ν cm$^{-1}$): 3012 (C-H aromatic), 2901, 2817 (C-H aliphatic), 1726 (C=O lactone), 1665 (C=O lactam), 1521 (C=C aromatic), 1425 (CON-O), 1353 (CO-O).

3-(adamantan-1-yl)-6-methyl-2-(3-nitrophenyl)-2,3-dihydro-1,3-oxazepin-4,7-dione (3a)

The reaction of imine (1a) (2.84 g, 0.01 mol) and citraconic anhydride (1.12 g, 0.01 mol) gave (3a) as a white powder, yield 3 g, 77%; mp 218–219°C. Found C$_{21}$H$_{25}$N$_2$O$_5$ (%): C 67.10, H 5.31, N 6.52. Calculated (%): C 66.65, H 6.10, N 7.07. $^1$H NMR (300 MHz, DMSO-d$_6$), δ, ppm: 10.12 (1H, s, O-CH-N); phenyl group (H$_a$, H$_b$, H$_g$ aromatic): 8.50 (1H, s, H$_d$), 8.32 (1H, d, J=9Hz, H$_e$), 8.21 (1H, d, J=6Hz, H$_f$), 7.78 (1H, t, J=12Hz, H$_g$), 6.02 (1H, d, J=9Hz, =C-CH-CO-N), 2.13 (3H, s, CH$_3$), adamantyl group: 2.06 (3H, s, 3CH$_3$), 1.53-2.02 (12H, m, 6CH$_2$). FTIR (ν cm$^{-1}$): 3058 (C-H aromatic), 2905, 2816 (C-H aliphatic), 1721 (C=O lactone), 274

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3-(adamantan-1-yl)-2-(3-bromophenyl)-1,3-oxazinan-6-one (4b)

The reaction of imine (1b) (3.18 g, 0.01 mol) and 3-chloropropanoic acid (1.08 g, 0.01 mol) gave (4b) as a white powder, yield 2.3 g, 61%; mp 174–175°C. Found C_{29}H_{22}BrNO_{3} (%): C 61.95, H 6.93, N 3.15. Calculated (%): C 61.54, H 6.20, N 3.59. 1H NMR (300 MHz, CDCl₃), δ ppm: 7.74 (1H, s, O-CH-N); phenyl group (H₂, H₅, H₆, H₇ aromatic): 6.94 (1H, d, J=9Hz), 6.56-6.61 (3H, m, H₄, H₆, H₇); 3.06 (2H, br.s, CH₂-N), 2.09 (2H, br.s, CH₃-CO), adamantyl group: 1.42 (3H, s, CH₃), 0.96-1.26 (12H, m, 6CH₃). FTIR (ν cm⁻¹): 3030 (C-H aromatic), 2912, 2825 (C-H aliphatic), 1723 (C=O lactone), 1638 (C=O lactam), 1531 (C=C aromatic), 1447 (CO-N), 1351 (CO-O).

The general procedure for synthesizing 3-(adamantan-1-yl)-2-(3-aryl)-1,3-oxazinan-6-one (5a, b)

A 0.01 mol solution of compound 1a and b was mixed with 15 mL dry 1,4-dioxane, and a convenient solution of 0.01 mol 3-mercaptopropanoic acid in 10 mL dry 1,4-dioxane in the presence of a small portion of anhydrous ZnCl₂. This was then refluxed for 22-24 hours with vigorous stirring. The solvent was vaporized and the residual solid was washed with a 5% solution NaHCO₃ and then with distilled water. The obtained product was dried and re-crystallized from EtOH.

Description of the properties of (5a and 5b)

3-(adamantan-1-yl)-2-(3-nitrophenyl)-1,3-thiazinan-4-one (5a)

The reaction of imine (1a) (2.84 g, 0.01 mol) and 3-mercaptopropanoic acid (1.06 g, 0.01 mol) gave (5a) as a white powder, yield 2.3 g, 64%; mp 290°C (decomp.). Found C_{29}H_{22}N₂O₃S (%): C 65.15, H 6.93, N 6.85, S 7.84. Calculated (%): C 64.49, H 6.49, N 7.52, S 8.61. FTIR (ν cm⁻¹): 3085 (C-H aromatic), 2939, 2813 (C-H aliphatic), 1709 (C=O lactam), 1549 (C=C aromatic), 832 (C-S-C).

3-(adamantan-1-yl)-2-(3-bromophenyl)-1,3-thiazinan-4-one (5b)

The reaction of imine (1b) (3.18 g, 0.01 mol) and 3-mercaptopropanoic acid (1.06 g, 0.01 mol) gave (5b) as a white powder, yield 2.7 g, 68%; mp 280°C (decomp.). Found C_{29}H_{22}BrN₂O₃S (%): C 60.05, H 6.44, N 3.82, S 8.54. Calculated (%): C 59.11, H 5.95, N 3.45, S 7.89. FTIR (ν cm⁻¹): 3059 (C-H aromatic), 2931, 2849 (C-H aliphatic), 1705 (C=O lactam), 1564 (C=C aromatic), 883 (C-S-C).
Table 3. FTIR spectral data (ν, cm⁻¹) for compounds (2a,b-5a,b)

| Comp.№ | ν C-H aromatic | ν C-H dihydropyrone | ν C=O lactone | ν C=O lactam | ν C=O aromatic | ν (CO)-N | ν (CO)-O | ν C-S-C |
|---------|----------------|---------------------|--------------|-------------|---------------|-----------|-----------|---------|
| 2a      | 3042           | 2907, 2846          | 1728         | 1685        | 1524          | 1436      | 1363      | -       |
| 2b      | 3012           | 2901, 2817          | 1726         | 1665        | 1521          | 1425      | 1353      | -       |
| 3a      | 3058           | 2905, 2816          | 1721         | 1673        | 1526          | 1441      | 1351      | -       |
| 3b      | 3019           | 2908, 2832          | 1723         | 1638        | 1531          | 1447      | 1351      | -       |
| 4a      | 3050           | 2929, 2847          | 1722         | -           | 1518          | -         | 1348      | -       |
| 4b      | 3030           | 2912, 2825          | 1719         | -           | 1523          | -         | 1340      | -       |
| 5a      | 3085           | 2939, 2813          | -            | 1709        | 1549          | -         | -         | 832     |
| 5b      | 3059           | 2931, 2849          | -            | 1705        | 1564          | -         | -         | 883     |

Table 4. ¹H NMR chemical shift (DMSO-d₆ and CDCl₃, δ, ppm) for compounds (2a,b-4a,b)

| Comp.№ | O-CH₃ | 4H-phenyl group | (15H-) adamantyl group (3H,3CH₃) | =CHCO-N | =CHCO-O (3H, CH₃) | CH₃-N | CH₂-CO |
|---------|-------|----------------|---------------------------------|---------|--------------------|-------|--------|
| 2a      | 10.15 (s) | 8.70 (1H, s, H₃) | 8.48-8.59 (1H, m, H₃) | 7.72-7.94 | 6.33 (1H, dd, J=6Hz, 12Hz) | 4.14 (1H, dd, J=9Hz, 6Hz) | - | - |
| 2b      | 9.86 (s) | 8.70 (1H, s, H₃) | 8.48-8.59 (1H, m, H₃) | 7.72-7.94 | 6.33 (1H, dd, J=6Hz, 12Hz) | 4.14 (1H, dd, J=9Hz, 6Hz) | - | - |
| 4a      | 7.93 (s) | 7.64 (1H, s, H₃) | 6.67-6.91 (3H, m, H₃) | 6.94 (1H, d, J=9Hz) | 6.06 (1H, d, J=9Hz) | - | - |
| 4b      | 7.74 (s) | 7.64 (1H, s, H₃) | 6.67-6.91 (3H, m, H₃) | 6.94 (1H, d, J=9Hz) | 6.06 (1H, d, J=9Hz) | - | - |

Results and Discussion:
The routes of the reactions are shown in reaction equation 1 and scheme 2. The reaction schemes included the synthesis of two new Schiff bases—(E)-N-(adamantan-1-yl)-1-(3-aryl)methanimine (1a,b)—which are essential for the dependent synthesis of three new imine derivatives—1,3-thiazinan-4-one, 1,3-oxazinan-6-one and 1,3-oxazepin-4,7-dione (2a,b-5a,b)—which contain an adamantyl fragment as a result of the condensation of compounds (1a,b) with 3-mercaptopropanoic acid, 3-chloropropanoic acid and maleic, citraconic anhydride, respectively. The structures of the intermediate and final products were determined by FTIR, ¹H NMR, C.H.N.S analysis, and single-crystal X-ray diffraction analysis for 1a. Details of the spectral data FTIR and ¹H NMR for products (1a,b-5a,b) and (1a,b-4a,b), respectively are displayed in Tables 2-4. An outline of the range of FTIR and ¹H NMR data will...
also be provided in the following reaction equation 1.

\[
\begin{align*}
\text{NH}_2 + \text{C}=\text{O} & \quad \text{heat 1-1.5 h} \quad \text{1a,b} \\
\end{align*}
\]

Reaction equation 1. For synthesis compounds (1a,b)

FTIR and \(^1\text{H}\) NMR data for compounds (1a,b) is shown in Figs. 1, 2, 3 and 4.

FTIR: all spectra exhibited evanescence in the stretching vibration bands of groups -NH\(_2\) and C=O for amine and aldehydes, respectively with characteristic stretching vibration bands of the azomethine group (C=N) at 1638 and 1631 cm\(^{-1}\), stretching vibration bands at range 3052 and 3092 cm\(^{-1}\) for C-H aromatic, and stretching vibration bands at range 2811-2906 cm\(^{-1}\) for C-H aliphatic. \(^1\text{H}\) NMR data: all spectra exhibited singlet and multiplet signals of the adamantyl group (3H, s, 3\text{CH}), (12H, m, 6\text{CH}_2) at the range \(\delta 1.63-2.13\) ppm, and protons for the CH=N group displayed a singlet signal at \(\delta 8.29\) and 8.58 ppm, and displayed singlet, doublet, doublet and triplet of protons (\(\text{H}_2\), \(\text{H}_6\), \(\text{H}_4\), \(\text{H}_5\) aromatic), respectively in an phenyl group at the range \(\delta 7.40-8.47\) ppm. The forming imine derivatives (1a,b) was carried out according to mechanism in literature (19). The nitrogen of amine attacks to the carbonyl group by nucleophilic addition to produce hemiaminal and then the leaving of a water molecule to give the target compound. See Scheme 1.

\[
\begin{align*}
\text{Ad}–\text{NH}_2 + \quad \text{Dipolar intermediate} \\
\rightarrow \text{Ad}–\text{N}+=\text{C}=\text{O} \\
\rightarrow \text{Ad}–\text{N}=\text{C}–\text{H} \\
\rightarrow \text{Ad}–\text{N}=\text{C}–\text{H} \\
\rightarrow \text{Ad}–\text{N}=\text{C}–\text{H} \\
\end{align*}
\]

Scheme 1. The suggested mechanism of the forming imine derivatives (1a,b)

![Figure 1. FTIR spectrum of compound (1a)](image1)

![Figure 2. FTIR spectrum of compound (1b)](image2)
Figure 3. $^1$H NMR spectrum of compound (1a)

Figure 4. $^1$H NMR spectrum of compound (1b)
FTIR spectra of compounds (2a,b-5a,b) revealed the disappearance of absorption bands of -C=N azomethines and C=O anhydrides, and the appearance of a stretching vibrations of C-H aromatic at 3010-3085 cm\(^{-1}\) and C-H\(_{\text{aliphatic}}\) at 2811-2915 cm\(^{-1}\). The stretching vibrations of the C=O\(_{\text{lactone}}\) and C=O\(_{\text{lactam}}\) groups were confirmed by a strong absorption band observed at the ranges 1722-1730 cm\(^{-1}\) and 1663-1704 cm\(^{-1}\) respectively, whilst the stretching vibrations of the CO-N, CO-O and C-S-C groups appeared at the frequency ranges of 1490-1529 cm\(^{-1}\), 1332-1340 cm\(^{-1}\) and 832-883 cm\(^{-1}\), respectively. These data was displayed selective spectra in Figs. 5, 6 and 7. The proposed mechanisms of formation 1,3-oxazepin-4,7-one (2a,b and 3a,b), 1,3-oxazinan-6-one (4a,b) and 1,3-thiazinan-4-one (5a,b) derivatives were explained in literatures (16, 21, 24). The forming mechanism (2a,b and 3a,b) compounds included a cycloaddition reaction (2+5) to produce cyclic seven membered by nucleophilic acts of the ion pair of electrons in an imine group towards the electrophilic center of carbonyl group of the cyclic anhydride to make cyclic four and five membered as a transition state [a] which was recycled intramolecular by concerted, breaking and forming cyclic seven membered to make the target compound [b] without forming intermediate. See Scheme 3.

While the mechanism forming compound (4a,b) may occur by concerting dipolar cycloaddition, which involves a Nucleophilic attack of the unshared electron pair-nitrogen atom of the azomethine group (-C=N-) towards a carbon atom of 3-chloropropanoic acid to which the chlorine...
atom binds to form an intermediate (carbocation), which recycled intramolecular to give the final product. See Scheme 4.

Scheme 4. The suggested mechanism of the forming 1,3-oxazinan-6-one derivatives (4a,b)

Whilst the mechanism forming compound (5a,b) may be occurred by addition anhydrous ZnCl₂ as catalyst which may activate the acid group by forming O...Zn bonding with oxygen carbonyl group, thereafter accelerate to promote nucleophilicity of mercapto group of 3-mercaptopropanoic acid causing its superficial addition on the imine. Then a nucleophile attacks of the electron pair-nitrogen atom towards the carbon atom of the carboxyl group. Afterwards support the intramolecular cyclo-addition to form intermediate and then the leaving water molecule. See Scheme 5.

Scheme 5. The suggested mechanism of the forming 1,3-thiazinan-4-one derivatives (5a,b)

Figure 5. FTIR spectrum of compound (3b)
The $^1$H NMR spectra of compounds (2a,b-4a,b) showed singlet and multiplet signals of the adamantyl group (3H, s, 3CH), (12H, m, 6CH$_2$) at the range $\delta$ 0.96-2.14 ppm, and protons for the O-CH$_2$N group displayed a singlet signal at range $\delta$ 7.74 -10.15 ppm, whilst protons of the phenyl group (H$_2$, H$_6$, H$_4$ H$_5$ aromatic) of compounds (2a,b-4a,b) showed different signals (s, m, m; s, d, d, t; d, m), respectively at a range of $\delta$ 6.56-8.70 ppm. The protons of the (=CH$_2$-N) and (=CH$_2$-CO) groups in compounds 4a,b displayed a broad singlet signals at ranges of 3.06-3.65 ppm and 2.09-2.10 ppm, respectively. These data was displayed selective spectra in Figs. 8, 9 and 10.
Figure 8. $^1$H NMR spectrum of compound (2a)

Figure 9. $^1$H NMR spectrum of compound (3b)
Crystallographic Study

The molecular structure of compound (1a) was displayed in Fig. 11. The crystalline data for (1a) was as follows: C_{17}H_{20}N_{2}O_{2}, MW= 284.35 g.mol^{-1}, Orthorhombic, space group (Pnma), a= 24.7642(7) Å, b= 6.8123(2) Å, c= 17.5235(5) Å, α= 90°, β= 90°, γ= 90°, V =2956.24(15) Å³, Z= 8, Crystal dimensions, mm (0.10 x 0.10 x 0.10), D_x= 1.278 g.cm⁻³.

The X-ray diffraction intensity for compound 1a was measured using a STOE StadiVari Pilatus100K diffractometer (26), λ(CuKα) = 1.5418 Å, using the ω-scanning technique. The data for the X-ray diffraction were processed by the WinGX suite (27), with the SHELX-97 program package being used to perform all subsequent calculations (28). The crystal structure was determined using the direct method, then refined with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were placed geometrically and refined isotropically using a riding model. The drawing of the structure was prepared using the MERCURY CSD 3.1 program (29). The bond length for (N1-C11) is 1.258 (3) Å, which is normal for double bond of (N=C), and the arrangement around this bond is trans (30). The structure displayed no hydrogen bonds. The details of the crystal data are provided in Tables 5-7.

Figure 10. ^1^H NMR spectrum of compound (4b)

Figure 11. The molecular structure, showing the atomic numbering of compound 1a
Table 5. Crystal data and refinement details for compound 1a

| Parameter                      | Value                           |
|--------------------------------|---------------------------------|
| Formula                        | C_{15}H_{28}N_{2}O_{2}          |
| MW                             | 284.35 g·mol⁻¹                 |
| Crystal system                 | Orthorhombic                    |
| Space Group                    | Pnma                            |
| a, Å                           | 24.7642(7)                     |
| b, Å                           | 6.8123(2)                      |
| c, Å                           | 17.5235(5)                     |
| α, °                           | 90                              |
| β, °                           | 90                              |
| γ, °                           | 90                              |
| V, Å³                          | 2956.24(15)                    |
| Z                              | 8                               |
| Dx, g/cm³                      | 1.278                           |
| Radiation                      | Cu Kα                          |
| μ(Kα, mm⁻¹)                    | 0.675                           |
| θ range, °                    | 3.569-72.124                   |
| h, k, l range                  | -30≤h≤30 -8≤k≤8 -21≤l≤21        |
| Crystal dimensions, mm         | 0.10 x 0.10 x 0.10             |
| Total reflections              | 30628                           |
| Reflections/parameters         | 3114 / 236                     |
| GooF                           | 0.956                           |
| R₁ [I≤2σ(I)]                  | 0.0394                          |
| Δρ_{max}/Δρ_{min} e/Å³         | 0.207/-0.159                   |

Table 6. Bond lengths d (Å) for compound 1a

| Bond                  | d (Å)  | Bond                  | d (Å)  |
|-----------------------|--------|-----------------------|--------|
| O1-N2                 | 1.212(3)| O21-N22               | 1.196(3)|
| O2-N2                 | 1.209(4)| O22-N22               | 1.207(3)|
| N1-C11                | 1.258(3)| N21-C31               | 1.258(3)|
| N1-C1                 | 1.466(3)| N21-C21               | 1.467(3)|
| N2-C14                | 1.470(4)| N22-C34               | 1.466(3)|
| C1-C2                 | 1.522(4)| C21-C22               | 1.524(3)|
| C1-C8                 | 1.530(2)| C21-C28               | 1.529(2)|
| C2-C3                 | 1.524(4)| C22-C23               | 1.525(4)|
| C2-H2A                | 0.9700  | C22-H22A              | 0.9700  |
| C2-H2B                | 0.9700  | C22-H22B              | 0.9700  |
| C3-C4                 | 1.519(3)| C23-C24               | 1.518(3)|
| C3-H3                 | 0.9800  | C23-H23               | 0.9800  |
| C4-C5                 | 1.511(3)| C24-C25               | 1.514(3)|
| C4-H4A                | 0.9700  | C24-H24A              | 0.9700  |
| C4-H4B                | 0.9700  | C24-H24B              | 0.9700  |
| C5-C6                 | 1.519(2)| C25-C26               | 1.517(2)|
| C5-C8                 | 1.528(2)| C25-C28               | 1.530(2)|
| C5-H5                 | 0.9800  | C25-H25               | 0.9800  |
| C6-H6A                | 0.9700  | C26-H26A              | 0.9700  |
| C6-H6B                | 0.9700  | C26-H26B              | 0.9700  |
| C8-H8A                | 0.9700  | C28-H28A              | 0.9700  |
| C8-H8B                | 0.9700  | C28-H28B              | 0.9700  |
| C11-C12               | 1.464(3)| C31-C32               | 1.464(3)|
| C11-H11               | 0.9300  | C31-H31               | 0.9300  |
| C12-C17               | 1.385(3)| C32-C33               | 1.390(3)|
| C12-C11               | 1.393(3)| C32-C37               | 1.392(3)|
| C13-C14               | 1.368(3)| C33-C34               | 1.369(3)|
| C13-H13               | 0.9300  | C33-H33               | 0.9300  |
| C14-C15               | 1.379(4)| C34-C35               | 1.382(4)|
| C15-C16               | 1.370(4)| C35-C36               | 1.374(4)|
| C15-H15               | 0.9300  | C35-H35               | 0.9300  |
| C16-C17               | 1.372(4)| C36-C37               | 1.377(4)|
| C16-H16               | 0.9300  | C36-H36               | 0.9300  |
| C17-H17               | 0.9300  | C37-H17               | 0.9300  |

Table 7. Bond angles ω° for compound 1a.

| Angle                  | ω°     |
|------------------------|--------|
| C11-N1-C1              | 121.5(2) |
| O2-N2-O1               | 123.3(3) |
| O2-N2-C14              | 117.4(3) |
| O1-N2-C14              | 119.3(3) |
| N1-C1-C2               | 116.6(2) |
| N1-C1-C8               | 107.06(13) |
| C2-C1-C8               | 108.77(13) |
| N1-C1-C8               | 107.06(13) |
| C2-C1-C8               | 108.77(13) |
| C8-C1-C8               | 108.3(2)  |
| C1-C2-C3               | 109.9(2)  |
| C4-C3-C4               | 109.5(3)  |
| C4-C3-C4               | 109.81(15) |
| C4-C3-C4               | 109.83(16) |
| C5-C4-C3               | 109.30(17) |
| C4-C5-C6               | 109.34(18) |
| C4-C5-C8               | 109.45(16) |
| C5-C6-C8               | 109.79(16) |
| C5-C6-C9               | 109.3(2)   |
| C5-C8-C11              | 110.25(14) |
| N1-C11-C12             | 122.9(2)  |
| C17-C12-C13            | 118.5(2)  |
| C17-C12-C11            | 121.0(2)  |
| C13-C12-C11            | 120.5(2)  |
| C14-C13-C12            | 118.9(2)  |
| C13-C14-C15            | 122.5(2)  |
| C13-C14-N2             | 118.2(3)  |
| C15-C14-N2             | 119.3(3)  |
| C16-C15-C14            | 118.6(2)  |
| C15-C16-C17            | 119.9(3)  |

Conclusion:
From the research undertaken here, two new starting materials (imines) of (E)-N-(adamantan-1-yl)-1-(3-aryl) methanimine were produced, with a yields of (91 and 94%) being obtained. These are precursors for the synthesis of three new imine derivatives—1,3-thiazinan-4-one, 1,3-oxazinan-6-one and 1,3-oxazepin-4,7-dione—which included an adamantyl fragment. All products were identified by ¹H NMR, FTIR spectra and C.H.N.S analysis, and the molecular structure of (E)-N-(adamantan-1-yl)-1-(3-nitrophenyl) methanimine was affirmed by X-ray crystallography.

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Conflicts of Interest: None.

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تحضير جزيئات سداسية وسباعية حلقية غير متجانسة حاوية على جزء الادامنتيل والاشعة السينية للتركيز البلوري لمركب (E)-N-(ادامانتان-1-يل)-1-(3-نايتروفينيل)ميثانيوم

علي سامي اسماعيل
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الخلاصة:
تضمن عملنا تحضير ثلاث مشتقات ايمينية جديدة، 1،1،3-ثيازينا-4 و 1،1،3-أوكسازينا-6 و 1،1،3-أوكسازيبين-4،7-دايس، والتي احتوت جزء الادامنتيل. وانتجت المركبات من خلال تفاعل تكليف قاعدة شيف (E)-N-(ادامانتان-1-يل)-1-(3-نايتروفينيل)ميثانيوم مع مركبات حمض البروبانويك وحيد، مالك، سيراتوكو الهيدرات، على التوالي. حضرت الايمينات الجديدة من خلال تفاعل التكليف للكيماويات-1-امين و3-نايترو، 3-برومو نيناليديدي في البيوتان الاعتيادي وحصلنا على نماذج جديدة، وشخص تركيبها باستخدام معالجات اشعة تحت الحمراء، الرنين النووي المغناطيسي البروتوني، والتحليل المكثف للعناصر (C.H.N.S). اثبت التركيب الجزئي للمركب (E)-N-(ادامانتان-1-يل)-1-(3-نايتروفينيل)ميثانيوم باستخدام تحليل الاشعة السينية للبلورات.

الكلمات المفتاحية: ادامانتان-1-يل امين، 1،1،3-أوكسازيبين-4،7-دايس، 1،1،3-أوكسازينا-6-ون، 1،1،3-ثيازينا-4-ون، الاشعة السينية للبلورات.