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Preparation and Identification of 1,3-Oxazepine Derivatives from Selected Carboxylic Acid Anhydrides with Imines Derived from 4-methyl aniline

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Abstract
Novel 1,3-oxazepine derivatives have been synthesis via (2+5) cycloaddition reaction of imines and selected cyclic carboxylic acid anhydrides by refluxing in dry benzene. Imines were prepared by thermal condensation of 4-methyl aniline and para substituted benzaldehyde in absolute ethanol under reflux conditions. The structure of the target compounds were identified by some physical properties and spectral data of FT-IR and ^{1}H-NMR.

Keywords: Imines, Carboxylic Acid Anhydrides. 1,3-Oxazepine.

الخلاصة
حضرت مشتقات جديدة من مركبات الأوكسازبين من تفاعل الإضافة الحلقية للإيمينات و إنهدريدات حوامض كاربوكسيلية حلقية مختارة بالتصعيد في البنزين الجاف . الإيمينات حضرت بواسطة التكاثف الحراري للأمين الأروماتي 4- مثيل أنيلين و معوضات البنزلديهايد في الموقع بارا تحت التصعيد في الإيثانول المطلق . تم تشخيص المركبات المستهدفة بإستخدام بعض الخصائص الفيزيائية والتحاليل الطيفية بواسطة الأشعة تحت الحمراء والرنين النووي المغناطيسي.

Introduction

Imines

Imines are organic compounds containing an azomethine group and identified by the general formula ($R^1R^2C=NR^3$) where R^1,R^2 and R^3 are alkyl, aryl, cyclo alkyl or heterocyclic groups [1]. They originally prepared by the German scientist Hugo Schiff in 1864 from the condensation of amino group in primary amines and amino acids with the carbonyl group in aldehydes or ketones, and therefor are known as Schiff bases [2]. The importance of imines is owing to their uses as key intermediates for organic synthesis [3][4][5][6][7], organometallic ligands [8], corrosion inhibitors [9], analytical reagents [10], growth controlling agent [11]. Most imines and their organometallic compounds exhibit significant biological activities [12], and medical uses such as anti-inflammatory, analgesic, antimicrobial, anticancer, antioxidant, anthelmintic and antidepressant activities [13].

Oxazepines

Oxazepines are a class of seven-membered heterocyclic ring compounds containing an oxygen atom at position 1 and a nitrogen atom in one of the three locations (2,3 or 4) in the heptane ring [14], they may contain carbonyl groups [15] and double bonds so they are known as unsaturated and non-aromatic [16]. 1,3-Oxazepine have been originally prepared via UV- irradiation of 4-phenyl-2-oxa-3-azabicyclo[3.2.0]-hepta-3,6-diene, ring expansion reaction of pyrylium tetraflouroborates and/or catalytic rearrangement of ketovinylaziridine [17]. Another route of their synthesis is based on the cycloaddition reaction (2+5) =7 between

imines and variety of carboxylic acid anhydrides [18].Most of the Oxazepines exhibit a wide range of biological activities and pharmaceutical applications such as anti-convulsant [19], anti-tumor and Colorectal Adenocarcinoma [18], anti-bacterial [20], anti-oxidant and anti-inflammatory [7], beside their uses as corrosion inhibitors [21], and liquid crystal components [22].

Experimental Analysis

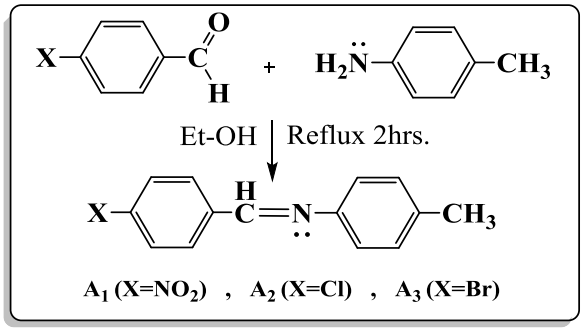
4-Methyl aniline, 4-nitro benzaldehyde, 4-chloro benzaldehyde, 4-bromo benzaldehyde, exo-3,6-epoxy-1,2,3,6-tetra-hydro phthallic anhydride, tetrachloro phthalic anhydride, and citraconic anhydride were supplied from Sigma-Aldrich and used directly without further purification, and all solvents were supplied from Scharlau and Romal. Melting points were recorded on Electro Thermal Melting Point Apparatus. FT-IR spectra were recorded on Bruker-Tensor 27 spectrophotometer in the range of 4000-400 cm^{-1} which was made at chemistry department, Anbar University, Iraq. ^{1}H-NMR spectra were recorded on Bruker-300 MHz spectrometer at Chemistry Department, Gazi University, Turkey. The chemical shifts of ^{1}H spectra were expressed as (δ) in ppm using Tetramethylsilane (TMS, δ= 0.00ppm) as internal standard and deuterated dimethyl sulfoxide (DMSO-d_6) as a solvent.

Synthesis of compounds

General procedure for synthesis of imines compunds [A_1-A_3].

A mixture of 4-methyl aniline (0.01 mol) and p-nitrobenzaldehyde (0.01 mol) in absolute ethanol (50 mL) with A few drops of glacial acetic acid as a catalyst was placed in round-bottom flask (100mL) with stirring. The reaction mixture was refluxed for 2hr and then left to cool down to room temperature, whereby, a solid product [A_1] was obtained. The solvent was removed by filteration and the residual solid was recrystallized twice from absolute ethanol. Other imine, **[A_2, A_3]**, were prepared from the reaction of equimolar amount of 4-methyl aniline with p-chlorobenzaldehyde or p-bromobenzaldehyde respectively using the same procedure [23].

The reaction pathway for the formation of Imine compounds [A_1-A_3] is depicted by scheme (1).



Scheme 1: Reaction pathway for the formation of Imine compounds [A_1-A_3].

Characterizations

(E)-N-(4-Nitrobenzylidene)-4-methyl aniline [A_1]:

Yellow solid, (97%yield), m.p. 108-110 °C, IR (ν cm^{-1}): 3099 cm^{-1} (C-H aromatic), 3048 cm^{-1} (C-H alkene), 2989-2833 cm^{-1} (C-H aliphatic), 1624 cm^{-1} (C=N), 1586-1462 cm^{-1} (C=C aromatic), 1501, 1326 cm^{-1} (C-NO_2).

(E)-N-(4-Chlorobenzylidene)-4-methyl aniline [A_2]:

White solid, (85%yield), m.p. 100-102 °C, IR (ν cm^{-1}): 3093 cm^{-1} (C-H aromatic), 3026 cm^{-1} (C-H alkene), 2984-2864 cm^{-1} (C-H aliphatic), 1620 cm^{-1} (C=N), 1575-1490 cm^{-1} (C=C aromatic), 826 cm^{-1} (C-Cl).

(E)-N-(4-Bromobenzylidene)-4-methyl aniline [A_3].

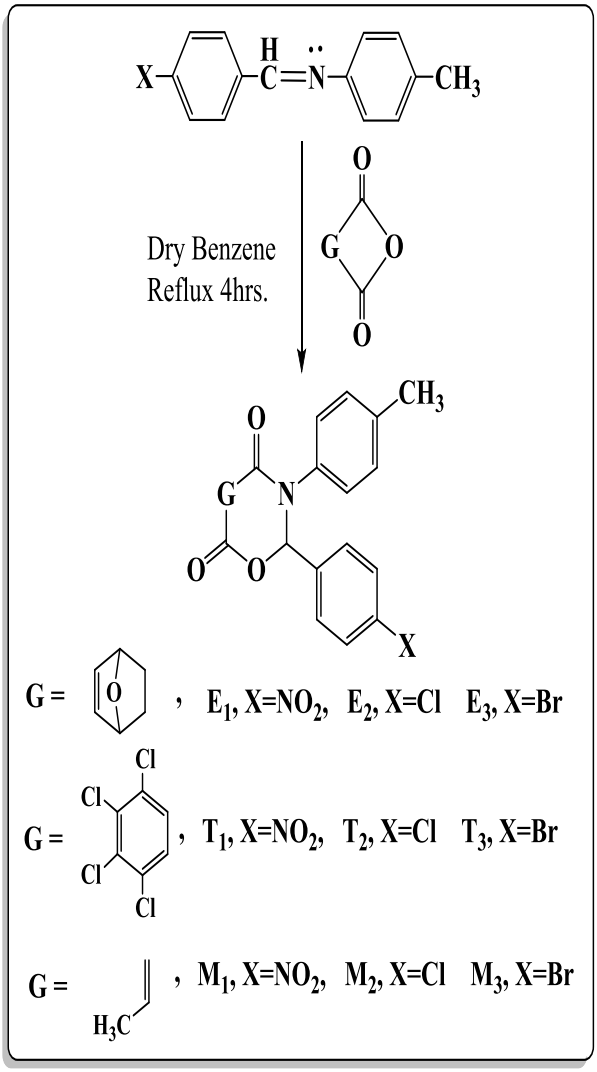
White solid, (83%yield), m.p. 116-118 °C, IR (ν cm^{-1}): 3089 cm^{-1} (C-H aromatic), 3025 cm^{-1} (C-H alkene), 2984-2864 cm^{-1} (C-H aliphatic), 1619 cm^{-1} (C=N), 1571-1489 cm^{-1} (C=C aromatic), 655 cm^{-1} (C-Br).

General procedure for 1,3-oxazepine derivatives [E_1-E_3, T_1-T_3, M_1-M_3].

In A round bottom flask (100 mL) equipped with double surface condenser fitted with an anhydrous calcium chloride guard tube and stirring magnetic bar, a mixture of Imines [A_1]/ [A_2]/ [A_3] (0.01 mol) and exo-3,6-epoxy-1,2,3,6-tetra-hydrophthallic anhydride (0.01

mol) in dry benzene (60 mL) was placed. The reaction mixture was refluxed for 4hr, then cooled down to the room temperature and let to stirrer on overnight. The separated solid product, [E_1], was filtered off, washed with $NaHCO_3$ solution (10 mL) then with distilled water, dried and recrystallized twice from dry benzene. Other derivatives [E_2, E_3, T_1, T_2, T_3, M_1, M_2, M_3] were prepared by reaction equimolar amount of tetrachlorophthallic anhydride or citraconic anhydride with imine [A_2], [A_3], [A_1], [A_2], [A_3], [A_1], [A_2], and [A_3] respectively [24].

The pathway of preparation of the target 1,3-oxazepine derivatives [E_1-E_3, T_1-T_3, M_1-M_3]were depicted in scheme (2).



Scheme 2: preparation pathway of 1, 3-oxazepine derivatives [E_1-E_3, T_1-T_3, M_1-M_3].

3-(4-Nitrophenyl)-4-(p-tolyl)-3,4,5a,6,9,9a-hexahydro-6,9-epoxybenzo[e][1,3]oxazepine-1,5-dione [E_1].

Pale yellow solid, (67% yield), m.p. 180-182 °C, IR (ν cm^{-1}): 3079 cm^{-1} (C-H aromatic), 2879 cm^{-1} (C-H aliphatic), 1694 cm^{-1} (C=O lactone), 1627 cm^{-1} (C=O lactam), 1498 cm^{-1} (C=C aromatic), 1297 cm^{-1} (C-N), 1017 cm^{-1} (C-O).

3-(4-Chlorophenyl)-4-(p-tolyl)-3,4,5a,6,9,9a-hexahydro-6,9-epoxybenzo[e][1,3]oxazepine-1,5-dione [E_2].

Pale yellow solid, (71%yield), m.p. 186-188 °C, IR (ν cm^{-1}): 3085 cm^{-1} (C-H aromatic), 2879 cm^{-1} (C-H aliphatic), 1695 cm^{-1} (C=O lactone), 1628 cm^{-1} (C=O lactam), 1500 cm^{-1} (C=C aromatic), 1265 cm^{-1} (C-N), 1001 cm^{-1} (C-O). ^{1}HNMR, δ=2.26 ppm [s, 3H, Aryl-CH_3], δ=6.48-6.28 ppm [m, 6H, oxo ring protons], δ=10.36 ppm [s, 1H, O-CH-N], δ=7.52-7.12 ppm [m, 8H, $H_{aromatic}$].

3-(4-Bromophenyl)-4-(p-tolyl)-3,4,5a,6,9,9a-hexahydro-6,9-epoxybenzo[e][1,3]oxazepine-1,5-dione [E_3].

Pale yellow solid, (78%yield), m.p. 184-186 °C, IR (ν cm^{-1}): 3077 cm^{-1} (C-H aromatic), 2879 cm^{-1} (C-H aliphatic), 1693 cm^{-1} (C=O lactone), 1627 cm^{-1} (C=O lactam), 1497 cm^{-1} (C=C aromatic), 1297 cm^{-1} (C-N), 1016 cm^{-1} (C-O). ^{1}HNMR, δ=2.26 ppm [s, 3H, Aryl-CH_3], δ=6.48-6.28 ppm [m, 6H, oxo ring protons], δ=10.36 ppm [s, 1H, O-CH-N], δ=7.52-7.12 ppm [m, 8H, $H_{aromatic}$].

6,7,8,9-Tetrachloro-3-(4-nitrophenyl)-4-(p-tolyl)-3,4-dihydrobenzo[e][1,3]oxazepine-1,5-dione [T_1].

Pale yellow solid, (67%yield), m.p. 180-182 °C, IR (ν cm^{-1}): 3043 cm^{-1} (C-H aromatic), 2920-2861 cm^{-1} (C-H aliphatic), 1718 cm^{-1} (C=O lactone), 1642 cm^{-1} (C=O lactam), 1603-1451 cm^{-1} (C=C aromatic), 1260 cm^{-1} (C-N), 1031 cm^{-1} (C-O). ^{1}HNMR, δ=2.28 ppm [s, 3H, Aryl-CH_3], δ=10.67 ppm [s, 1H, O-CH-N], δ=8.38-7.15 ppm [m, 8H, $H_{aromatic}$].

6,7,8,9-Tetrachloro-3-(4-chlorophenyl)-4-(p-tolyl)-3,4-dihydrobenzo[e][1,3]oxazepine-1,5-dione [T_2].

Pale yellow solid, (70%yield), m.p. 172-174 °C, IR (ν cm^{-1}): 3035 cm^{-1} (C-H aromatic), 2921-2862 cm^{-1} (C-H aliphatic), 1707 cm^{-1} (C=O lactone), 1646 cm^{-1} (C=O lactam), 1599-1513 cm^{-1} (C=C aromatic), 1262 cm^{-1} (C-N), 1022 cm^{-1} (C-O).

6,7,8,9-Tetrachloro-3-(4-bromophenyl)-4-(p-tolyl)-3,4-dihydrobenzo[e][1,3]oxazepine-1,5-dione [T_3].

Pale yellow solid, (67%yield), m.p. 180-182 °C, IR (ν cm^{-1}): 3031 cm^{-1} (C-H aromatic), 2918-2862 cm^{-1} (C-H aliphatic), 1706 cm^{-1} (C=O lactone), 1644 cm^{-1} (C=O lactam), 1600-1445 cm^{-1} (C=C aromatic), 1260 cm^{-1} (C-N), 1017 cm^{-1} (C-O). ^{1}HNMR, δ=2.28 ppm [s, 3H, Aryl-CH_3], δ=10.70 ppm [s, 1H, O-CH-N], δ=7.50-6.59ppm [m, 8H, $H_{aromatic}$].

Methyl-2-(4-nitrophenyl)-3-(p-tolyl)-2,3-dihydro-1,3-oxazepine-4,7-dione [M_1].

Pale yellow solid, (68% yield), m.p. 174-176 °C, IR (ν cm^{-1}): 3026 cm^{-1} (C-H aromatic), 2920-2871 cm^{-1} (C-H aliphatic), 1694 cm^{-1} (C=O lactone), 1628 cm^{-1} (C=O lactam), 1480 cm^{-1} (C=C aromatic), 1212 cm^{-1} (C-N), 1032 cm^{-1} (C-O).

Methyl-2-(4-chlorophenyl)-3-(p-tolyl)-2,3-dihydro-1,3-oxazepine-4,7-dione [M_2].

Pale yellow solid, (68% yield), m.p. 174-176 °C, IR (ν cm^{-1}): 3026 cm^{-1} (C-H aromatic), 2920-2872 cm^{-1} (C-H aliphatic), 1694 cm^{-1} (C=O lactone), 1629 cm^{-1} (C=O lactam), 1479 cm^{-1} (C=C aromatic), 1213 cm^{-1} (C-N), 1036 cm^{-1} (C-O). ^{1}HNMR, δ=1.98 ppm [s, 3H, Aryl-CH_3], δ=2.25 ppm [s, 3H, Het-CH_3], δ=6.09 ppm [s, 3H, Het-H], δ=10.08 ppm [s, 1H, O-CH-N], δ=7.50-7.09 ppm [m, 8H, $H_{aromatic}$].

Methyl-2-(4-bromophenyl)-3-(p-tolyl)-2,3-dihydro-1,3-oxazepine-4,7-dione [M_3].

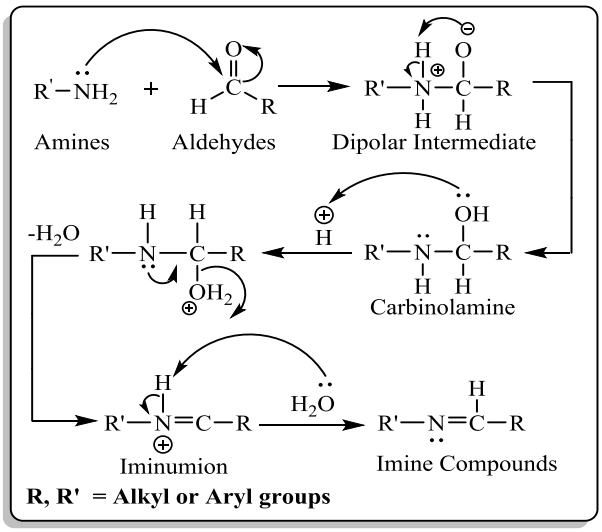
Pale yellow solid, (69% yield), m.p. 172-174 °C, IR (ν cm^{-1}): 3027 cm^{-1} (C-H aromatic), 2921-2872 cm^{-1} (C-H aliphatic), 1695 cm^{-1} (C=O lactone), 1630 cm^{-1} (C=O lactam), 1479 cm^{-1} (C=C aromatic), 1213 cm^{-1} (C-N), 1037 cm^{-1} (C-O). ^{1}HNMR, δ=1.98 ppm [s, 3H, Aryl-CH_3], δ=2.25 ppm [s, 3H, Het-CH_3], δ=6.09 ppm [s, 3H, Het-H], δ=10.08 ppm [s,1H, O-CH-N], δ=7.50-7.09 ppm [m, 8H, $H_{aromatic}$].

Results and Discussion

Imines were prepared by thermal condensation reaction of 4-methyl aniline with p-nitro, p-chloro and p-bromo benzaldehydes in absolute ethanol under reflux condition and used as starting materials for the synthesis of Oxazepine derivatives. The products were characterized by confirming their structure by some physical properties and FT-IR spectra.

The FT-IR spectra of compounds [A_1-A_3] showed that the disappearance of the stretching frequency absorption bands of (-NH_2) And (C=O) groups for amines and aldehydes respectively and the appearance of characteristic absorption bands at (3099-3089 cm^{-1}) due to (C-H) aromatic, at (3048-3025 cm^{-1}) due to (=C-H) alkene, at (2989-2833 cm^{-1}) due to (C-H) aliphatic, at (1624-1619 cm^{-1}) due to (C=N) imine groups, and (C=C) of the aromatic ring at (1586-1462 cm^{-1}) [25]. See Table 1.

The formation of imine compounds is thoroughly explained by literature [26], and the general mechanism is suggested to take place by nucleophilic addition of the amino group to the carbonyl group associated with formation of hemiaminal, followed by rejection of water to give the product as shown in scheme (3).

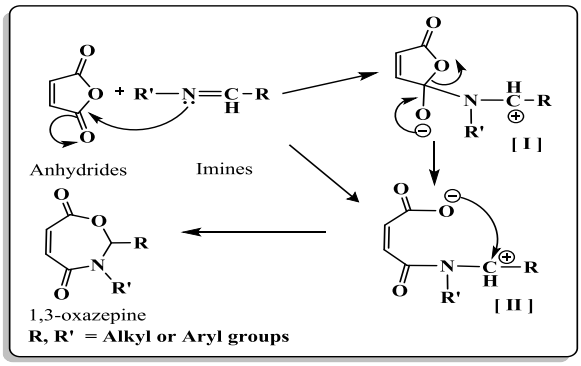


Scheme 3: Proposed mechanism for the formation of Imine compounds.

Oxazepine derivatives prepared in this paper were by cycloaddition reaction [2+5] of the prepared imines with each of tetrachlorophthalic, citraconic and exo-3,6-epoxy-1,2,3,6-tetra-hydrophthallic anhydride by refluxing the reaction mixture in dry benzene.

FT-IR Spectra for 1,3-Oxazepine derivatives showed that the disappearance of absorption bands of (-C=N) and (C=O) groups of imines and carboxylic acid anhydrides respectively and appearance of the stretching absorption bands of aromatic (C-H) at (3085-3026 cm^{-1}), aliphatic (C-H) at (2921-2861 cm^{-1}), lactone (C=O) at (1718-1693 cm^{-1}), lactam (C=O) at (1646-1627 cm^{-1}), aromatic ring (C=C) at (1603-1445 cm^{-1}), (C-N) at (1212-1297 cm^{-1}) and (C-O) at (1001-1037 cm^{-1}) respectively [27] as shown in figures (1-3) for selected compounds. See Table 2.

The reaction is proposed to proceed via nucleophilic attack of the ioan pair of electrons in the mild nucleophilic imino group on the electrophilic carbonyl group of the cyclic anhydride to produce a dipolar intermediate [I] which then collapses to give intermediate [II] or to form intermediate [II] directly. Then intermediate [II] internally recyclized to give the target molecule [20]. The plausible mechanism for formation of 1,3-oxazepine derivatives can be illustrated by scheme (4).



Scheme 4: The plausible mechanism of formation of Oxazepine derivatives.

The ^{1}H-NMR spectra of the selected derivative [E_3] showed significant signals : 2.28 ppm (m, 2H, CH-CH of oxo- ring), 2.35 ppm (signals for CH_3-Ar and CH-O-CH of oxo- ring overlapping with signal of DMSO-d6 solvent), 6.28-6.48 (dd, 2H, HC=CH), 7.12-7.15 ppm (dd, 4H, Ar-CH_3), 7.48-7.52 ppm (dd, 4H, Ar-Br), and 10.36 ppm (s, 1H, N-CH-O). The discussion for derivative [T_2] is following: 2.28 ppm (s, 3H, CH_3-Ar), 6.59-6.91 ppm (dd, 4H, Ar-CH_3), 7.13-7.50 ppm (dd, 4H, Ar-Cl), and 10.70 ppm (s, 1H, N-CH-O). The discussion for derivative [M_2] is following:1.98 ppm (s, 3H, CH_3-Ar), 2.25 ppm (s, 3H, CH_3), 6.08 (s, 1H, HC-C=C), 7.09-7.12 ppm (dd, 4H, Ar-CH_3), 7.48-7.60 ppm (dd, 4H, Ar-Cl), and 10.08 ppm (s, 1H, N-CH-O) [28] as shown in figures (4-6) for selected compounds. Other derivatives [E_2], [T_1] and [M_3] are tabulated in Table 3.

Finally, the spectral data of both FT-IR and ^{1}H.NMR of the prepared compounds are quite consistent with the literature which confirm a successful recyclization of the dipolar intermediate to form 1,3-oxazepine ring.

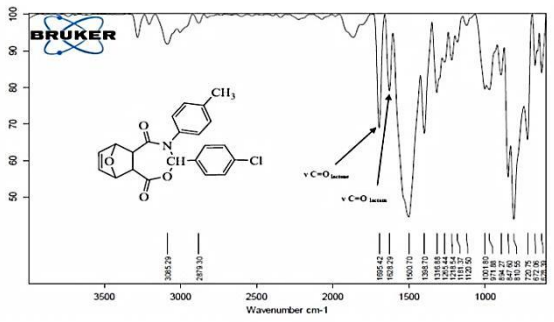


Figure 1: FT-IR spectrum for Compound [E_2].

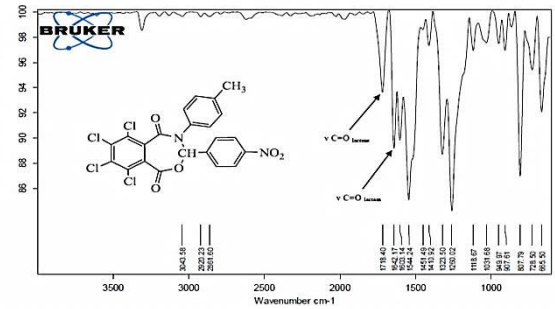


Figure 2: FT-IR spectrum for Compound [T_1].

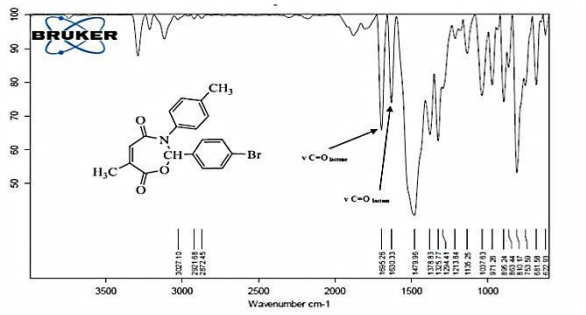


Figure 3: FT-IR spectrum for Compound [M_3].

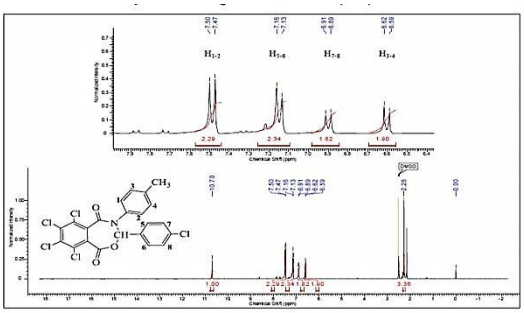


Figure 5: ^{1}H-NMR spectrum for Compound [T_2].

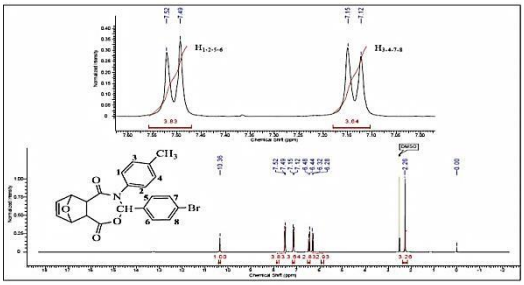


Figure 4: ^{1}H-NMR spectrum for Compound [E_3].

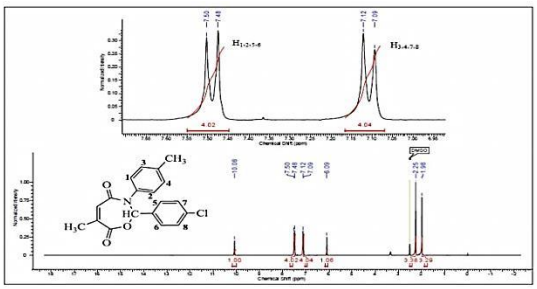


Figure 6: ^{1}H-NMR spectrum for Compound [M_2].

Table 1: FT-IR spectral data (cm^{-1}) for synthesized compounds [A_1-A_3].

Comp.	C-H $_{aro.}$	=C-H $_{alk.}$	C-H $_{ali.}$	C=N $_{imi.}$	C=C $_{aro.}$	C-X $_{sub.}$
A_1	3099	3048	2989-2833	1624	1586-1462	1501,1326
A_2	3093	3026	2984-2864	1620	1575-1490	826
A_3	3089	3025	2984-2864	1619	1571-1489	655

Table 2: FT-IR spectral data (cm^{-1}) for synthesized [E_1-E_3], [T_1-T_3] and [M_1-M_3] compounds.

Comp.	C-H $_{aro.}$	C-H $_{ali.}$	C=O $_{lactone}$	C=O $_{lactam}$	C=C $_{aro.}$	C-N	C-O
E_1	3079	2879	1694	1627	1498	1297	1017
E_2	3085	2879	1695	1628	1500	1265	1001
E_3	3077	2879	1693	1627	1497	1297	1016
T_1	3043	2920-2861	1718	1642	1603-1451	1260	1031
T_2	3031	2921-2862	1707	1646	1599-1513	1262	1022
T_3	3031	2918-2862	1706	1644	1600-1445	1260	1017
M_1	3026	2920-2871	1694	1628	1480	1212	1032
M_2	3026	2920-2872	1694	1629	1479	1213	1036
M_3	3027	2921-2872	1695	1630	1479	1213	1037

Table 3: ^{1}H-NMR chemical shift (ppm) for synthesized [E_2, E_3], [T_1, T_3] and [M_2, M_3] compounds.

Comp.	(s,3H)	(s,1H)	$H_{aromatic\ rings}$	Other group
E_2	2.26	10.36	7.52-7.12	H, oxo ring protons = 6.48-6.28
E_3	2.26	10.36	7.52-7.12	H, oxo ring protons = 6.48-6.28
T_1	2.28	10.67	8.38-7.15	---
T_3	2.28	10.70	7.50-6.59	---
M_2	1.98	10.08	7.50-7.09	(Het-CH_3 = 2.25), (Het-H = 6.09)
M_3	1.98	10.08	7.50-7.09	(Het-CH_3 = 2.25), (Het-H = 6.09)

Conclusion

A successful achievement of cycloaddition reaction of imines to carboxylic acid anhydrides to give 1,3-oxazepine ring is obtained. The expected plausible reaction mechanism was suggested according to the spectral data of FT-IR and ^{1}HNMR which is consistent with formation of charged linear intermediate in the transition state which then collapses via internal cyclization reaction to produce the target molecule.

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