Simple One-Step Syntheses of Heterocyclic Systems from (4*Z*)-2-Phenyl-4-(thien-2-ylmethylene)-1,3(4*H*)-oxazol-5-one

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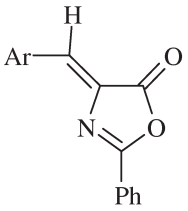
The title compound (*Ia*) was synthesized and its (*Z*)-configuration was assigned. The present investigation was intended to study the behaviour of *Ia* towards nitrogen, carbon, and oxygen nucleophiles. Thus, reaction of *Ia* with *p*-toluidine in ethanol or in acetic acid afforded the thienylaminomethylidene-(4*H*)-oxazol-5-one and alkenamide without oxazolone ring together with the imidazolinone, respectively. Hydrazinolysis and azidolysis of *Ia* resulted in the vinylthiophene and tetrazole derivatives. The triazine and oxadiazinone were obtained upon the effect of phenylhydrazine and hydroxylamine on *Ia,* respectively. When compound *Ia* was allowed to react with carbon nucleophiles, namely phenylmagnesium bromide or dry benzene under Friedel—Crafts conditions, it gave the acylated product benzoylaminovinylthiophene whereas the ester thienylpropenoate was obtained from the reaction of *Ia* with sodium ethoxide. In the absence of aromatic hydrocarbon and in tetrachloroethane as inert solvent containing anhydrous $AlCl_3$, *Ia* underwent intramolecular alkylation and/or acylation to afford the respective thieno[3,2-*c*]pyridine and cyclopentadieno[*b*]thiophene respectively.

In continuation to the previous study on heterocyclic compounds [1—7] and because of the fact that 4-arylidene-(4*H*)-oxazol-5-one and its derivatives exhibit good anticonvulsant [8], bactericidal [9, 10], fungicidal [9], and insecticidal activities [10], the present work was aimed to synthesize new 4-ylidene-(4*H*)-oxazol-5-ones of expected biological activity and explore their behaviour towards different nitrogen, carbon, and oxygen nucleophilic species in order to achieve heterocyclic transformations. Interest in the chemistry of the azlactones continues unabated because of their usefulness as intermediates in the synthesis of different heterocyclic compounds or modified α-amino acids or their derivatives [11—14].

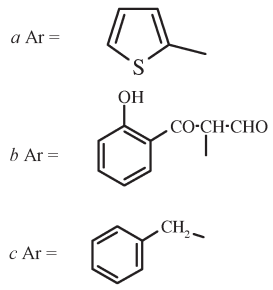
In 1975 [11], it was reported that when aldehydes were condensed with hippuric acid in the presence of acetic anhydride containing anhydrous sodium acetate, usually one isomer of 4-ylideneazlactone was obtained, the configuration of this isomer has not been discussed. Recently, *Beccalli et al.* [15] synthesized different 4-ylidene-(4*H*)-oxazol-5-ones and assigned their spatial arrangement as *Z*-configuration.

In the present work, new 4-ylidene-2-phenyl-1,3-(4*H*)-oxazol-5-ones *Ia*—*Ic* were synthesized *via* the reaction of hippuric acid with thiophene-2-carboxaldehyde, 3-formylchromone or phenylacetaldehyde under Perkin—Erlenmeyer reaction conditions. The spatial arrangement of these compounds has been established by comparing their ^{1}H NMR spectra for the vinylic proton which was found to be at δ = 7.52. This is in agreement with the *Z*-configuration reported by Beccalli. Thus, the *Z*-configuration on the double bond of the synthesized oxazolones was assigned by analogy with the literature. This seems to be credible due to that the steric repulsion in the *Z*-configuration is less than in *E*-isomer.



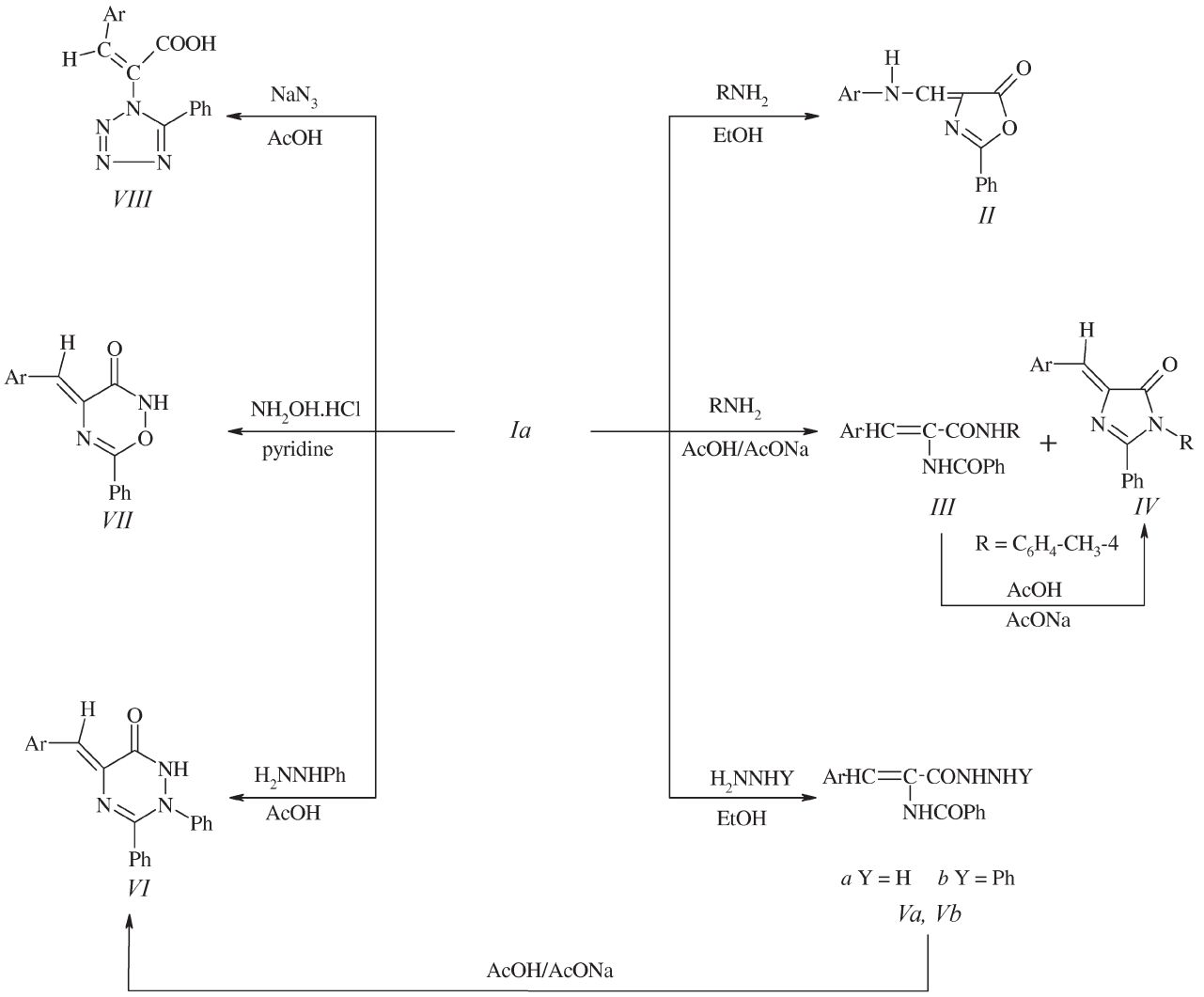
I

Z-configuration



The fission of the 1,5-bond of 2-oxazolin-5-ones by amines has been reported [12, 16—18] to give alkenamide derivatives and its application is useful in the synthesis of *N*-substituted amides.

The effect of primary aromatic amines, namely *p*-toluidine on the oxazolinone *Ia* was reinvestigated. Thus treatment of substrate *Ia* with *p*-toluidine in refluxing ethanol afforded the thienylaminomethylidene-(4*H*)-oxazol-5-one *II* (*cf.* Scheme 1), contrary to what was reported [12]. Compound *II* was formed through the attack of the amino group on the electron-deficient methylidene carbon atom followed by dearylation of *p*-tolyl moiety and migration of thiophene ring to the ni-

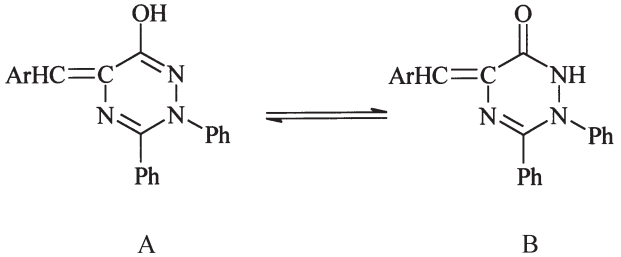


Scheme 1

trogen atom. On the other hand, the aminolysis of the oxazolone *Ia* with the same amine in refluxing acetic acid—fused anhydrous sodium acetate mixture [7, 19] resulted in the formation of 2-imidazolin-5-one *IV* (77 %) which deposited on cooling. Upon dilution of the mother liquor of the reaction mixture, the alkenamide *III* (10 % yield) was obtained as a nonreported additional product. The structural features of both *III* and *IV* were established from their IR and ^{1}H NMR spectra. It seems that formation of *IV* proceeded *via* cyclization of *III* obtained by 1,5-bond cleavage of the azlactone moiety from the nucleophilic attack by the amine. This was verified by refluxing *III* in the acetic acid—sodium acetate mixture to yield *IV*.

Several nitrogen nucleophilic species like Schiff bases [20], benzalazine [20], and ethyl glycinate chloride [21] were reported to attack the oxazolone leading to 1,5-bond cleavage. This prompted the author to study the effect of hydrazines, namely hydrazine hydrate, phenylhydrazine, hydroxylammonium chloride or sodium azide on the azlactone *Ia*.

Compound *Ia* reacted with hydrazine hydrate or phenylhydrazine in ethanol to yield the hydrazides *Va* and *Vb*, respectively. On the other hand, phenylhydrazine reacted with *Ia* in refluxing acetic acid and sodium acetate to afford 2,3-diphenyl-5-(thien-2-ylmethylene)-2,5-dihydro-1*H*-1,2,4-triazin-6-one *VI* which was also obtained by cyclization of the hydrazide *Vb* by heating it under reflux in acetic acid



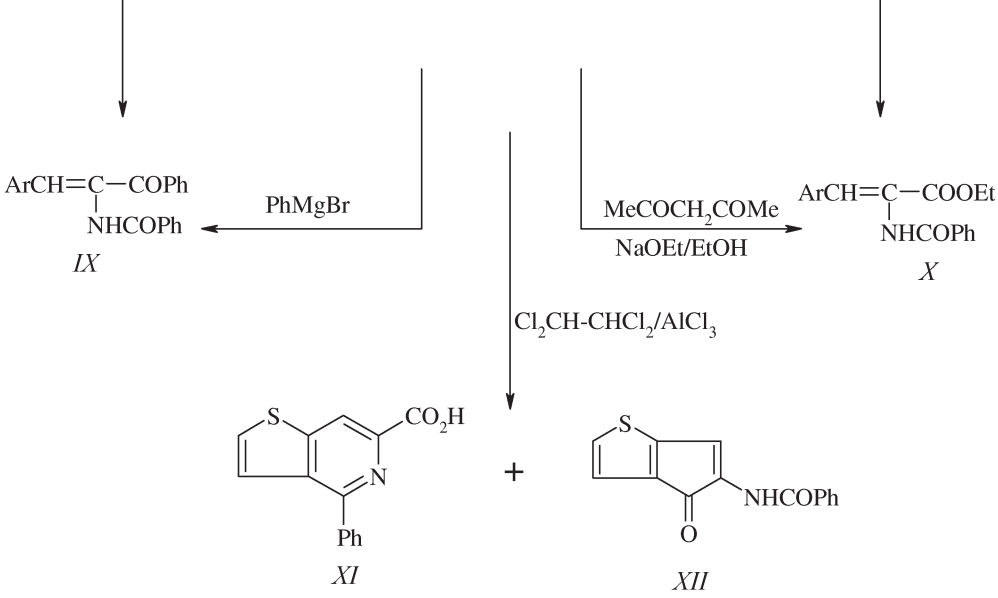
containing anhydrous sodium acetate. Compound *VI* could be present in lactam—lactim dynamic equilibrium (A and B) but the lactam form is thermodynamically more stable due to the fact that the oxo form is more stabilized by 54.4 kJ mol^{-1} than the enol form [22].

It has been reported [23] that the reaction of hydroxylammonium chloride with azlactones in refluxing pyridine afforded 1-hydroxy-2-imidazolin-5-one. In the present work, when the azlactone *Ia* was allowed to react with the mentioned reagent under the same conditions, ring-expansion occurred to give the oxadiazinone *VII*. The structure of the latter compound was exclusively substantiated from the IR spectrum which showed ν(CO) of oxadiazinone rather than ν(CO) of imidazolinone, in addition to the absence of ν(OH) of 1-hydroxyimidazolinone. The ^{1}H NMR spectrum of compound *VII* exhibited two singlets attributable to the presence of NH/OH of lactam—lactim structure.

The azidolysis of *Ia* by sodium azide in acetic acid involves cleavage of 1,2-bond to give the tetrazole *VIII* contrary to the normal 1,5-ring cleavage of the oxazolinone ring by all other nitrogen nucleophiles, *viz.* amines and hydrazines. The *E*-configuration of C=C bond of tetrazole derivative *VIII* was assigned from its ^{1}H NMR since the carboxylic proton exhibited a doublet due to splitting by the vinylic proton. The measured coupling constant was found to be 2.0 Hz which is compatible with that of *E*-configuration of acrylic acid [24].

The second approach of investigation involved the reaction of the oxazolinone ring with different carbon nucleophiles. Thus when compound *Ia* was allowed to react with phenylmagnesium bromide under Grignard reaction conditions and dry benzene under Friedel—Crafts reaction conditions, it afforded the same acylated product: 2-[2-benzoyl-2-(benzoylamino)vinyl]thiophene *IX* (*cf.* Scheme 2).

The structure of compound *IX* was rigidly established by identity of the product (melting point, mixed melting point, IR spectra and TLC). On the other hand, to obtain the polyfunctionalized vinylthiophenes C and D, the azlactone *Ia* was allowed to react with typical active methylene-containing compounds, namely acetylacetone and ethyl acetoacetate in the presence of ethanolic sodium ethoxide as basic catalyst under Michael's reaction conditions [25]. The formation of the adducts C and D would involve the cleavage of the heterocyclic ring of *Ia via* the attack of the carbanion formed from the active methylene group. Surprisingly, the same product was obtained, instead of C and D and its structure was



Scheme 2

substantiated as ethyl 2-(benzoylamino)-3-(thien-2-yl)propenoate *X* which was formed through the attack of ethoxide ion leading to cleavage of oxazolone ring. It has been reported that the attack of oxygen nucleophiles like 2-dimethylaminoethanol, in the presence of sodium alcoholate, on oxazolone ring resulted in ring cleavage [26]. In inert solvents like 1,1,2,2-tetrachloroethane under Friedel—Crafts reaction conditions, compound *Ia* underwent intramolecular alkylation and/or acylation to afford thieno[3,2-*c*]pyridine *XI* and cyclopentadieno[*b*]thiophene *XII,* respectively. Compound *XI* is formed by alkyl-oxygen fission followed by ring closure whereas compound *XII* is formed by acyl-oxygen fission followed by ring closure *via* the internal attack of the acylium ion on the thiophene ring.

EXPERIMENTAL

All melting points reported are uncorrected and were determined on a Stuart electric melting point apparatus. Elemental analysis gave satisfactory results: w_i(found)/w_i(calc.): C ± 0.44 %, H ± 0.22 %, N ± 0.34 %. The IR spectra were measured on a Unicam 1200 spectrometer or Mattson infinity series FT-IR using KBr wafer technique. The ^{1}H NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solutions on Varian Gemini 200 MHz instrument using TMS as internal standard with chemical shifts δ from downfield to upfield. Mass spectrum of the starting azlactone *Ia* was recorded on Shimadzu GC-MS-QP 1000 EX instrument operating at 70 eV. TLC was performed on ready-to-use silica gel plates Merck 60. Physical characteristics of the synthesized compounds are given in Table 1.

Table 1. Physical Characteristics of Synthesized Compounds

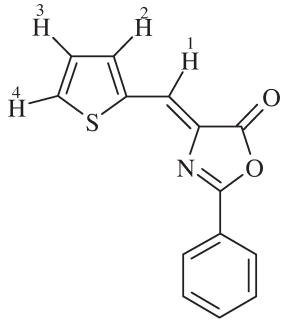
Compound	M.p./℃	Solvent	Yield/%	Colour
Ia	168—169	L.P.[a]	70	Bright yellow
Ib	174—176	L.P.	82	Bright yellow
Ic	163	E	75	Yellow
II	173—175	E	78	Pale yellow
III	237	B	10	Pale yellow
IV	192—193	E	77	Yellow
Va	177—179	T—E	87	Pale yellow
Vb	185—186	Aq. E	55	Pale yellow
VI	220—222	B	60	Bright yellow
VII	228 (decomp.)	Aq. E	52	Brownish yellow
VIII	206 (decomp.)	B—E	50	Pale brown
IX	135 (decomp.)	L.P.—B	68	Pale brown
X	170	L.P.—B	90	Colourless
XI	182	E	45	Yellow
XII	> 300	P	36	Deep brown

a) L.P. = light petroleum (80—100 ℃), E = ethanol, T = toluene, B = benzene, P = pyridine.

(4*Z*)-2-Phenyl-4-(thien-2-ylmethylene)-1,3(4*H*)-oxazol-5-one (*Ia*—*Ic*)

An equimolar mixture of hippuric acid and suitable aldehyde (15 mmol) in freshly distilled acetic anhydride (10 cm^3) containing fused anhydrous sodium acetate (1.2 g) was heated on a steam bath for 3 h and then cooled. The yellow solid, which was formed during heating, was filtered off, washed with light petroleum (40—60 ℃), well dried, triturated with cold saturated sodium carbonate solution, filtered again, washed with water, dried and recrystallized from suitable solvent to yield *Ia*—*Ic* (*cf.* Table 1). The azlactone *Ia* was prepared by the condensation of α-thiophenealdehyde diethyl acetal with hippuric acid [27].

Ia: IR spectrum, $\tilde{\nu}$/cm^{-1}: 3088 (H_{arom}), 2926 (H_{aliph}), 1792 (CO), 1649 (C═N). ^{1}H NMR spectrum ($CDCl_3$), δ: 7.48—8.20 (m, 5H, H_{arom}), 7.73 (d, 1H, $J_{3,4}$ = 5.2 Hz, H-4), 7.63 (d, 1H, $J_{2,3}$ = 3.8 Hz, H-2), 7.52 (s, 1H, H-1), 7.16 (dd, 1H, $J_{2,3}$ = 3.8 Hz, $J_{3,4}$ = 5.2 Hz, H-3). MS, m/z (I_r/%): 255 ($M^{+\bullet}$, 27.08), 256 $(M + 1]^{+\bullet}$, 5.68), 150 (0.02), 106 (8.36), 105 (100), 78 (5.99), 77 (8.16).



Ib: IR spectrum, $\tilde{\nu}$/cm^{-1}: 1795 ($CO_{azlactone}$), 1710 ($CO_{aldehyde}$), 1675 ($CO_{aromatic\,ketone}$), 1618 (C═N). ^{1}H NMR spectrum ($CDCl_3$), δ: 9.71 (s. 1H, OH), 8.30 (d, 1H, J = 1.6 Hz, O═C<u>H</u>), 8.26 (d, 1H, J = 1.6 Hz, C<u>H</u>═C), 8.14 (dd, J = 1.4 Hz and 1.6 Hz, 1H, COC<u>H</u>(CHO)CH═), 7.46—7.74 (m, 9H, H_{arom}).

Ic: IR spectrum, $\tilde{\nu}$/cm^{-1}: 3132 and 3096 (H_{arom}), 2984 (H_{aliph}), 1786 ($CO_{azlactone}$). ^{1}H NMR spectrum ($CDCl_3$), δ: 7.25—7.52 (m, 10H, H_{arom}), 6.95 (t, J = 12 Hz, 1H, vinylic proton), 3.40 (d, J = 12 Hz, 2H, —CH_2—).

2-Phenyl-4-(thien-2-ylaminomethylidene)-(4*H*)-oxazol-5-one (*II*)

A mixture of oxazolone *Ia* (2.55 g; 10 mmol) and *p*-toluidine (1.07 g; 10 mmol) was refluxed in ethanol (80 cm^3) for 2 h. The yellow solid product obtained

on cooling was filtered off, washed with ethanol, dried and recrystallized.

IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3410 (NH br), 1792 ($CO_{azlactone}$), 1643 (C═N). ^{1}H NMR spectrum ($CDCl_3$), δ: 7.49—8.20 (m, 5H, H_{arom}), 7.76 (d, 1H, $J_{3,4}$ = 5.2 Hz, H-4), 7.60 (d, 1H, $J_{2,3}$ = 3.8 Hz, H-2), 7.50 (s, 1H, H-1), 7.17 (dd, 1H, $J_{2,3}$ = 3.8 Hz, $J_{3,4}$ = 5.2 Hz, H-3), 1.96 (s, 1H, NH, exchangeable).

2-{Benzoylamino-2-[*N*-(4-methylphenyl)-carbamoyl]vinyl}thiophene (*III*) and 1-(4-Methylphenyl)-2-phenyl-4-(thien-2-ylmethylene)-2-imidazolin-5-one (*IV*)

An equimolar mixture of compound *Ia* and *p*-toluidine (10 mmol) was heated under reflux in acetic acid (30 cm^3) containing fused anhydrous sodium acetate (0.3 g) for 3 h. The solid that deposited after cooling the reaction mixture was filtered off, washed with acetic acid, dried and recrystallized to yield the imidazolinone (*IV*). Upon diluting the mother liquor of the reaction mixture a crude solid was separated out. Filtration of the latter afforded a solid which gave the alkenamide *III* on recrystallization (*cf.* Table 1).

III: IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3289 and 3238 (two NH), 3069 (H_{arom}), 1660 and 1641 (two CO_{amide}). ^{1}H NMR spectrum (DMSO-d_6), δ: 9.36 (s, 1H, CONH—C_6H_5), 9.08 (s, 1H, NHCO—$C_6H_4CH_3$), 7.03—8.13 (m, 9H, H_{arom}), 7.71 (d, 1H, $J_{3,4}$ = 5.8 Hz, H-4), 7.52 (d, 1H, $J_{2,3}$ = 4.0 Hz, H-2), 7.51 (s, 1H, H-1), 7.29 (dd, 1H, $J_{2,3}$ = 4.0 Hz, $J_{3,4}$ = 5.8 Hz), 2.28 (s, 3H, CH_3).

IV: IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3072 and 3038 ($H_{arom}$), 1707 (CO), 1634 (C═N). ^{1}H NMR spectrum (DMSO-d_6) δ: 7.46—8.36 (m, 9H, H_{arom}), 7.68 (d, 1H, $J_{3,4}$ = 5.1 Hz, H-4), 7.59 (d, 1H, $J_{2,3}$ = 3.7 Hz, H-2), 7.43 (s, 1H, H-1), 7.21 (dd, 1H, $J_{2,3}$ = 3.7 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 2.10 (s, 3H, CH_3).

2-[2-Aminocarbamoyl)-2-benzoylaminovinyl]-thiophene (*Va*) and 2-[*N*-Phenylamino-carbamoyl)-2-benzoylaminovinyl]thiophene (*Vb*)

A solution of compound *Ia* (10 mmol) in ethanol (50 cm^3) was treated with hydrazine hydrate (10 mmol) or phenylhydrazine (10 mmol) and refluxed for 3 h, then left to cool. Diluting the reaction mixture with water gave a crude solid which was filtered off, washed with water, dried and recrystallized to give *Va*. In case of *Vb*, the reaction mixture yielded the crude product as yellow crystalline needles upon cooling without dilution.

Va: IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3315 and 3209 ($NH_2$), 3069 ($H_{arom}$), 1670 ($CO_{hydrazide}$), 1645 ($CO_{amide}$). ^{1}H NMR spectrum ($CDCl_3$), δ: 7.06—8.01 (m, 5H, H_{arom}), 7.66 (s br, 1H, NH—CO—), 7.62 (d, 1H, $J_{3,4}$ = 5.2 Hz, H-4), 7.60 (d, 1H, $J_{2,3}$ = 3.6 Hz, H-2), 7.53 (s, 1H, H-1), 7.08 (dd, 1H, $J_{2,3}$ = 3.6 Hz, $J_{3,4}$ = 5.2 Hz, H-3), 4.0 (s br, 1H, NHNH$_2$), 1.60 (s br, 2H, —NHNH$_2$).

Vb: IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3328 and 3236 ($NH_2$), 3080 ($H_{arom}$), 1674 ($CO_{hydrazide}$), 1650 ($CO_{amide}$).

2,3-Diphenyl-5-(thien-2-ylmethylene)-2,5-dihydro-(1*H*)-1,2,4-triazin-6-one (*VI*)

Method A

A solution of oxazolone *Ia* (10 mmol) in acetic acid (60 cm^3) was treated with phenylhydrazine (10 mmol) and refluxed for 3 h in the presence of fused anhydrous sodium acetate (0.3 g). The solid that separated after cooling was crystallized from benzene. IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3261 (NH), 3084 and 3051 (H_{arom}), 2926 (H_{aliph}), 1699 (CO), 1630 (C═N). ^{1}H NMR spectrum ($CDCl_3$), δ: 7.21—8.35 and 6.64—6.97 (m, 10H, H_{arom}), 7.71 (d, 1H, $J_{3,4}$ = 5.0 Hz, H-4), 7.59 (d, 1H, $J_{2,3}$ = 3.6 Hz, H-2), 7.52 (s, 1H, H-1), 7.37 (s, 1H, NH), 7.14 (dd, 1H, $J_{2,3}$ = 3.6 Hz, $J_{3,4}$ = 5.0 Hz, H-3).

Method B

Fused anhydrous sodium acetate (1.0 g) was added to a solution of *Vb* (10 mmol) in acetic acid (50 cm^3) and the reaction mixture was heated under reflux for 1 h and the solid obtained upon cooling was crystallized.

6-Phenyl-4-(thien-2-ylmethylene)-2,3-dihydro-1,2,5-oxadiazin-3-one (*VII*)

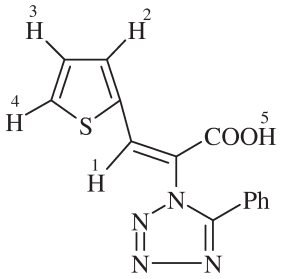
An equimolar mixture of oxazolone *Ia* and hydroxylammonium chloride (10 mmol) was heated under reflux in pyridine (30 cm^3). The reaction solution was left to cool, then it was poured into ice-hydrochloric acid and the precipitate was filtered off, washed with cold water, dried and crystallized.

IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3230 (NH), 3076 ($H_{arom}$), 2907 ($H_{aliph}$), 1703 (CO), 1641 (C═N). ^{1}H NMR spectrum (DMSO-d_6), δ: 10.97 (s, 1H, NH), 7.47—8.39 (m, 5H, H_{arom}), 7.71 (d, 1H, $J_{3,4}$ = 5.2 Hz, H-4), 7.69 (d, 1H, $J_{2,3}$ = 3.8 Hz, H-2), 7.50 (s, 1H, H-1), 7.14 (dd, 1H, $J_{2,3}$ = 3.8 Hz, $J_{3,4}$ = 5.2 Hz, H-3), 2.85 (s, 1H, OH).

1-[1-Carboxy-2-(thien-2-yl)vinyl]-5-phenyl-tetrazole (*VIII*)

A solution of compound *Ia* (10 mmol) in acetic acid (30 cm^3) was treated with sodium azide (2.6 g; 40 mmol) dissolved in the least amount of water, then refluxed for 3 h, left to cool and poured onto crushed ice with stirring. The solid deposited was filtered off by suction, washed thoroughly with cold water, dried and crystallized.

IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3447 (OH br), 3092 ($H_{arom}$), 2829 ($H_{aliph}$), 1695 ($CO_{acid}$), 1611 (C═N). ^{1}H NMR spectrum ($CDCl_3$), δ: 8.34 (d, J = 2.0 Hz, 1H, H-5)



[24], 7.06—7.79 (m, 5H, H_{arom}), 7.75 (d, 1H, $J_{3,4}$ = 5.4 Hz, H-4), 7.58 (d, 1H, $J_{2,3}$ = 3.6 Hz, H-2), 7.51 (s, 1H, H-1), 7.12 (dd, 1H, $J_{2,3}$ = 3.6 Hz, $J_{3,4}$ = 5.4 Hz, H-3).

2-[2-Benzoyl-2-(benzoylamino)vinyl]thiophene (*IX*)

Method A

To an ethereal solution of phenylmagnesium bromide prepared from magnesium (0.97 g) and bromobenzene (40 mmol) in dry ether (100 cm^3) a suspension of compound *Ia* (10 mmol) in dry ether (50 cm^3) was added dropwise. The reaction mixture was heated under reflux for 3 h and decomposed with cold saturated ammonium chloride solution. The organic layer was dried by anhydrous magnesium sulfate and evaporated to give the crude product which was crystallized.

Method B

Anhydrous aluminium chloride (4.0 g; 30 mmol) was added to a vigorously stirred solution of the azlactone *Ia* (10 mmol) in dry benzene (40 cm^3), then the reaction mixture was heated on boiling water bath for 8 h, allowed to stand at room temperature overnight, then it was added to ice-hydrochloric acid (50 cm^3). The organic layer was separated, washed with water and the excess benzene was removed by steam distillation. The organic material was extracted with ether, dried by anhydrous magnesium sulfate, then ether was distilled off to obtain the crude product which was crystallized. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3330 (br, NH/OH), 3069 (H_{arom}), 2930 (H_{aliph}), 1680 (CO_{ketone}), 1634 (CO_{amide}). ^{1}H NMR spectrum (DMSO-d_6), δ: 9.58 (s, 1H, NH), 6.94—7.84 (m, 10H, H_{arom}), 7.59 (d, 1H, $J_{3,4}$ = 5.5 Hz, H-4), 7.44 (d, 1H, $J_{2,3}$ = 4.1 Hz, H-2), 6.97 (dd, 1H, $J_{2,3}$ = 4.1 Hz, $J_{3,4}$ = 5.5 Hz, H-3), 6.40 (s, 1H, H-1).

Ethyl 2-(Benzoylamino)-3-(thien-2-yl)-propenoate (*X*)

Method A

An equimolar mixture of oxazolone *Ia* (10 mmol) and acetylacetone (1.0 cm^3) or ethyl acetoacetate (1.3 cm^3) was treated with sodium ethoxide (1.36 g; 20 mmol) in absolute ethanol (40 cm^3). The reaction mixture was stirred at room temperature for 20 h, diluted with water and then acidified with diluted hydrochloric acid to get the crude white product which was crystallized.

Method B

A solution of compound *Ia* (10 mmol) in absolute ethanol (40 cm^3) was added to a solution of sodium ethoxide in absolute ethanol (0.46 g of sodium metal in 10 cm^3 of ethanol). The reaction mixture was stirred at room temperature for 20 h and worked out as in method *A*.

IR spectrum, $\tilde{\nu}/cm^{-1}$: 3254 (br, NH/OH), 3069 (H_{arom}), 2941 (H_{aliph}), 1711 (CO_{ester}), 1657 (CO_{amide}). ^{1}H NMR spectrum ($CDCl_3$), δ: 7.06—7.98 (m, 5H, H_{arom}), 7.86 (s, 1H, NH), 7.58 (d, 1H, $J_{3,4}$ = 5.1 Hz, H-4), 7.55 (d, 1H, $J_{2,3}$ = 3.8 Hz, H-2), 7.49 (s, 1H, H-1), 7.09 (dd, 1H, $J_{2,3}$ = 3.8 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 4.30 (q, 2H, J = 7.2 Hz, —C$\underline{H}_2$CH$_3$), 1.32 (t, 3H, J = 7.2 Hz, —CH$_2$C$\underline{H}_3$).

7-Phenylthieno[3,2-*c*]pyridin-2-carboxylic Acid (*XI*) and 5-Benzoylamino-4-oxo-cyclopentadieno[*b*]thiophene (*XII*)

A solution of oxazolone *Ia* (10 mmol) in 1,1,2,2-tetrachloroethane (50 cm^3) was added during 30 min at room temperature to a stirred suspension of anhydrous aluminium chloride (12.0 g; 90 mmol) in the same solvent (50 cm^3). The reaction mixture was stirred for further 2 h, heated on a boiling water bath for 6 h and left to stand overnight, hydrolyzed with hydrochloric acid—ice and steam-distilled to get rid of the excess solvent. The crude material was crystallized from ethanol to give *XI* and ethanol-insoluble part was crystallized from pyridine to afford *XII*.

XI: IR spectrum, $\tilde{\nu}/cm^{-1}$: 3320 (br, OH), 3129 and 3089 (H_{arom}), 1710 (CO_{acid}), 1635 (C═N). ^{1}H NMR spectrum ($CDCl_3$), δ: 10.92 (s, 1H, COO$\underline{H}$), 9.25 (s, 1H, pyridine proton), 8.76 (d, 1H, J = 6.2 Hz, —S—C$\underline{H}$), 8.52 (d, 1H, J = 6.2 Hz, S—CH═C$\underline{H}$), 7.42—8.20 (m, 5H, H_{arom}).

XII: IR spectrum, $\tilde{\nu}/cm^{-1}$: 3290 (NH), 3114 and 3086 (H_{arom}), 1734 ($CO_{cyclic\,ketone}$), 1663 (CO_{amide}). ^{1}H NMR spectrum ($CDCl_3$), δ: 8.72 (d, 1H, J = 6.1 Hz, S—C$\underline{H}$), 8.45 (d, 1H, J = 6.1 Hz, S—CH═C$\underline{H}$), 7.45—8.29 (m, 5H, H_{arom}), 7.90 (s, 1H, NH), 5.49 (s, 1H, C$\underline{H}$═C—CO—).

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