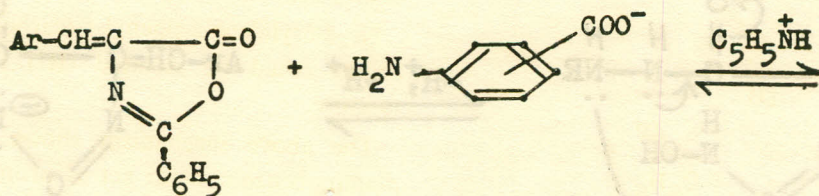
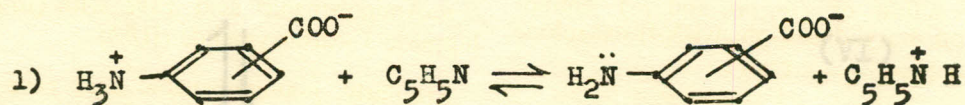
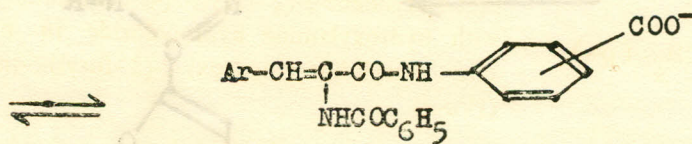
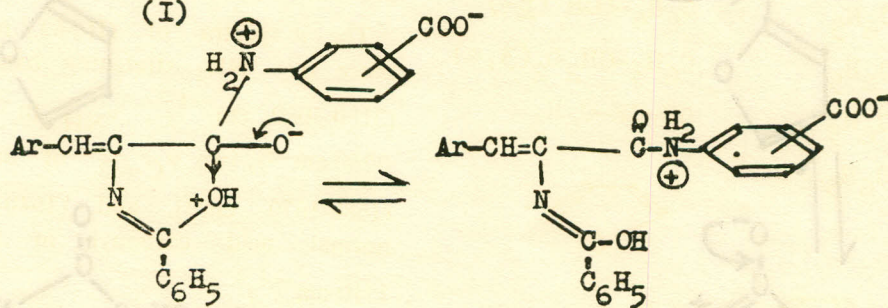


(III)

The reaction possibly takes place according to the following mechanism. (Scheme 1)

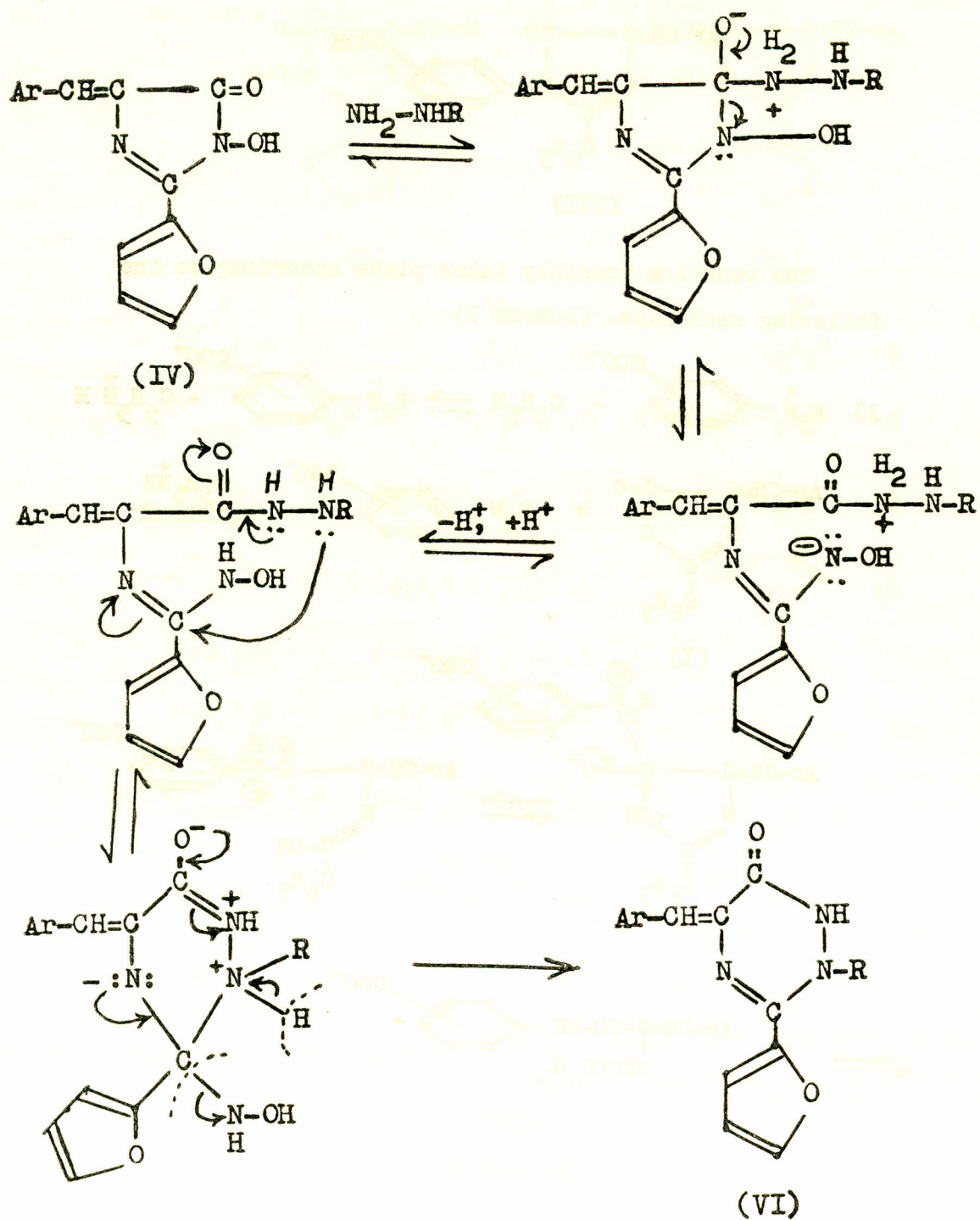


(I)

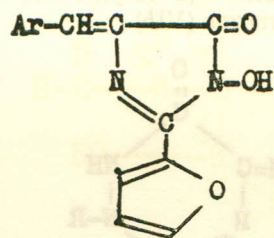


(II)

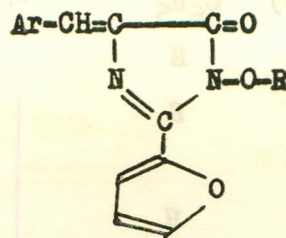
(Scheme 1)



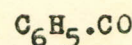
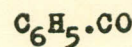
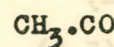
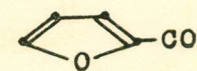
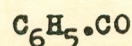
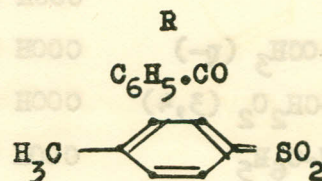
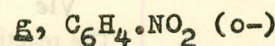
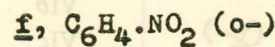
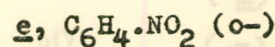
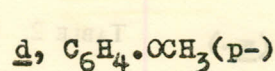
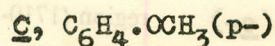
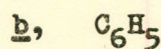
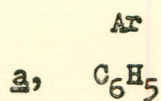
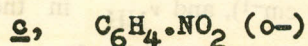
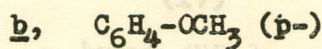
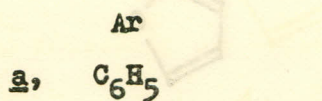
(Scheme 2)



(IV)



(V)



The ir spectral data of (V) showed a doublet for $\nu_{C=O}$'s of imidazolone ring in the regions (1760-1730 cm^{-1}) and (1665-1640 $^{-1}$) and

$\nu_{C=O}$ for ester in the region (1825-1770 cm^{-1}) (cf. Table 1).

Reaction of 4-arylidene-1-hydroxy-2-furyl-5-imidazolone (IV) with benzene and chloroform (V) and (VI) with acetic acid and chloroform (VII) for the preparation of 4-arylidene-1-hydroxy-2-furyl-5-imidazolone (IV).

In the present investigation, the hitherto unknown reaction of 4-arylidene-1-hydroxy-2-furyl-5-imidazolone (IV) with hydrazine was discovered.




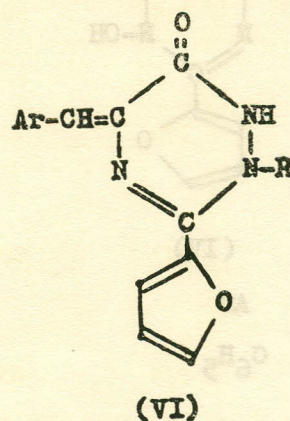
Ar	R
a. $C_6H_4 \cdot OCH_3$ (p-)	H
b. $C_6H_4 \cdot OCH_3$ (p-)	C_6H_5
c. $C_6H_4 \cdot Cl$ (o-)	H
d. $C_6H_4 \cdot NO_2$	H
e. 	H
Ar	X
a: C_6H_5	COOH (o-)
b: $C_6H_4 \cdot OCH_3$ (p-)	COOH (o-)
c: $C_6H_3 \cdot CH_2O_2$ (3,4)	COOH (o-)
d: $CH=CH \cdot C_6H_5$	COOH (o-)
e: 	COOH (o-)
f: C_6H_5	COOH (m-)
g: $C_6H_4 \cdot OCH_3$ (p-)	COOH (m-)
h: $C_6H_3 \cdot CH_2O_2$ (3,4)	COOH (m-)
i: C_6H_5	COOH (p-)
j: $C_6H_5 \cdot CH=CH$	COOH (p-)
k: 	COOH (p-)

TABLE 1. IR SPECTRAL DATA FOR 4-ARYLIDENE-1-AROXYLOXY-2-(2'-FURYL)-5-IMIDAZOLONE (V).

Compound No.	$\nu_{C=O}$ of imidazolone cm^{-1}	$\nu_{C=O}$ of ester cm^{-1}
Va	1735, 1650	1780
Vb	1750, 1655	—
Vc	1730, 1645	1770
Vd	1735, 1650	1795
Ve	1750, 1665	1825
Vf	1750, 1650	1780
Vg	1760, 1650	—
Vh	1730, 1640	1775

In the present investigation, the hitherto unknown reaction of 4-arylidene-1-hydroxy-2-(2'-furyl)-5-imidazolone (IV) with hydrazines was discovered.

Thus, 4-arylidene-1-hydroxy-2-(2'-furyl)-5-imidazolone (IV) reacts with hydrazines and/or phenylhydrazine in ethanol or acetic acid to give 4-arylidene-6-(2'-furyl)-3-oxo-1,2,3-trihydro-1,2,5-triazines (VIa, c, d, and e) and 4-arylidene-6-(2'-furyl)-3-oxo-1-phenyl-2,3-dihydro-1,2,5-triazine (VIb).



The ir spectra of (VI) showed $\nu_{C=O}$ in the region (1710-1660 cm^{-1}), and ν_{NH} in the region (3430-3140 cm^{-1}) (broad) (cf. Table 2).

TABLE 2. IR SPECTRAL DATA FOR TRIAZINES (VI).

Compound No.	$\nu_{C=O}$ cm^{-1}	ν_{NH} cm^{-1}
VIa	1660	3420-3140
VIb	1710	3270
VIc	1680	3420-3280
VId	1670	3430-3220
VIe	1675	3420-3210

The reaction possibly takes place according to the following scheme (Scheme 2).

Experimental Procedure

Melting points are not corrected; ir spectra were measured with Perkin-Elmer Infrared Model 137, and Unicam SP 1200 Infrared Spectrophotometer using the KBr wafer technique.

Action of Amino Benzoic Acids on 4-Arylidene-2-Phenyl-5(4)-oxazolones (Ia-e)/(Formation of (IIa-k). A solution of 4-arylidene-2-phenyl-5(4)-oxazolone (Ia-e) (0.1 mole) in pyridine was treated with aromatic amino acid (0.1 mole) and the reaction mixture was refluxed for (3 hr.), then cooled and poured on crushed ice and then treated with ice-cold HCl. The precipitated product was filtered off, and recrystallized from suitable solvents (cf. Table 3).

Reaction of 4-Arylidene-1-hydroxy-2-(2'-furyl)-5-imidazolone (IVa, b, d and e) with acid chlorides; Formation of 4-arylidene-1-aroxyloxy-2-(2'-furyl)-5-imidazolone (Va-h).

TABLE 3. FORMATION OF ARYLIDENE-HIPPURIC CARBOXYANILIDES (IIa-k).

Products	M.P. °C	Yield	Solvent of crystalli- zation	M.F.	Analysis (%)	
					Req.	Found
IIa	208	80	E	C ₂₃ H ₁₈ N ₂ O ₄	C, 71.49 H, 4.7 N, 7.25	71.85 5.01 7.49
IIb	240	70	E	C ₂₄ H ₂₀ N ₂ O ₅	C, 69.22 H, 4.84 N, 6.73	69.09 5.0 6.52
IIc	242	80	E	C ₂₄ H ₁₈ N ₂ O ₆	C, 66.97 H, 4.22 N, 6.51	66.69 4.36 6.49
II d	235	65	E	C ₂₅ H ₂₀ N ₂ O ₄	C, 72.8 H, 4.89 N, 6.79	72.83 5.04 6.51
IIe	170	70	E	C ₂₁ H ₁₆ N ₂ O ₅	C, 67.01 H, 4.29 N, 7.44	66.99 4.07 7.64
II f	248-51	75	E	C ₂₃ H ₁₈ N ₂ O ₄	C, 71.49 H, 4.7 N, 7.25	71.63 4.52 7.35
IIg	239-41	80	E	C ₂₄ H ₂₀ N ₂ O ₅	C, 69.22 H, 4.84 N, 6.73	68.94 5.08 6.66
IIh	231	70	M	C ₂₄ H ₁₈ N ₂ O ₆	C, 66.97 H, 4.22 N, 6.51	66.65 4.40 6.32
IIi	230	80	M	C ₂₃ H ₁₈ N ₂ O ₄	C, 71.49 H, 4.70 N, 7.25	71.77 4.85 7.51
IIj	246	70	M	C ₂₅ H ₂₀ N ₂ O ₄	C, 72.8 H, 4.89 N, 6.79	72.61 4.80 6.47
IIk	240	70	M	C ₂₁ H ₁₆ N ₂ O ₅	C, 67.01 H, 4.29 N, 7.44	66.93 4.50 7.61

E=ethanol; m=methanol

TABLE 4. FORMATION OF 4-ARYLIDENE-1-AROXYLOXY-2(2'-FURYL)-5-IMIDAZOLONE (Va-h).

Product	M.P. °C	Yield	Solvent of crystalli- zation	M.F.	Analysis (%)	
					Req.	Found
Va	175-8	71	E	C ₂₁ H ₁₄ N ₂ O ₄	C, 70.38	70.97
					H, 3.93	4.28
					N, 7.81	7.34
Vb	151	31	*	C ₂₁ H ₁₆ N ₂ SO ₅	C, 61.75	61.94
					H, 3.94	4.34
					N, 6.85	6.54
Vc	180-1	92	A	C ₂₂ H ₁₆ N ₂ O ₅	C, 68.03	68.51
					H, 4.15	4.42
					N, 7.21	6.80
Vd	178-9	76	E	C ₂₀ H ₁₄ N ₂ O ₆	C, 63.49	63.52
					H, 3.72	3.74
					N, 7.40	7.35
Ve	162-4	45	*	C ₁₆ H ₁₁ N ₃ O ₆	C, 56.30	56.44
					H, 3.24	3.62
					N, 12.31	11.69
Vf	160	75	E	C ₂₁ H ₁₃ N ₃ O ₆	C, 62.53	62.94
					H, 3.24	3.69
					N, 10.41	9.86
Vg	154-5	33	*	C ₂₁ H ₁₅ N ₃ SO ₇	C, 55.62	55.96
					H, 3.33	3.54
					N, 9.26	8.86
Vh	182-3	87	M	C ₁₉ H ₁₂ N ₂ O ₅	C, 65.51	65.42
					H, 3.47	4.00
					N, 8.04	7.57

A=acetic acid; E=ethanol; M=methanol; and
*decomposes on crystallization

TABLE 5. FORMATION OF TRIAZINES (VIa-e).

Products	M.P. °C	Yield	Solvent of crystalli- zation	M.F.	Analysis (%)	
					Req.	Found
VIa	318-21	20	B/M	C ₁₅ H ₁₃ N ₃ O ₃	C, 63.59	63.73
					H, 4.62	4.67
					N, 14.83	14.65
VIb	210-2	47	E	C ₂₁ H ₁₇ N ₃ O ₃	C, 70.18	70.76
					H, 4.76	5.04
					N, 11.69	11.23
VIc	206	20	E	C ₁₄ H ₁₀ N ₃ ClO ₂	C, 58.44	58.98
					H, 3.50	3.99
					N, 14.60	15.36
VI d	206-7	61	B	C ₁₄ H ₁₀ N ₄ O ₄	C, 56.37	56.16
					H, 3.35	3.67
					N, 18.78	18.71
VIe	223-5	61	E	C ₁₂ H ₉ N ₃ O ₃	C, 59.25	59.47
					H, 3.72	4.14
					N, 17.27	16.99

B=benzene; E=ethanol; and M=methanol

A solution of (IVa, b, d and/or e) (0.1 mole) in chloroform and a few drops of pyridine was treated with acetyl, benzoyl, furoyl, and/or *p*-toluenesulphonyl chlorides (0.1 mole) in chloroform at room temperature; the reaction mixture was left to evaporate. The solid products were recrystallized from the proper solvent to give (Va-h) (cf. Table 4).

Hydrazinolysis of (IVb-e): Formation of (VIa-e).

A solution of imidazolone (IVb-e) (0.1 mole) in ethanol or acetic acid was treated with hydrazine hydrate (excess) or phenylhydrazine (0.1 mole). The reaction mixture was heated under reflux for 3 hr., then cooled. The solid products were filtered

off and recrystallized from suitable solvent to the corresponding triazines (VIa-e) (cf. Table 5).

References

1. A. F. M. Fahmy, and M. O. A. Orabi, *Indian J. Chem.*, **10**, 961 (1972).
2. R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, London, (1967) p. 97.
3. A. F. M. Fahmy, A. A. Afifi, and I. G. Shenouda, *J. Chem. U. A. R.* (accepted for publication).

data and its spectrum which shows ν_{NH} at 3300-3500 cm^{-1} .

Structure (III) was confirmed from (V) analytical data, (W) its spectrum which shows ν_{NH} at 3200-3400 cm^{-1} (br) and (X) authentically via the reaction of aniline with benzalazine (Ib) in the presence of anhydrous AlCl_3 .

It was found also that ethylbenzoate undergoes base catalyzed 1,4-cycloaddition with benzylidene acetophenone and (V) via two competitive routes to give 1,4,6-triphenyl-3-cyano-2(H)-pyridine (VI) in major yield, and ethyl-2-amino-1,4,6-triphenyl-dihydropyridinate (VII).

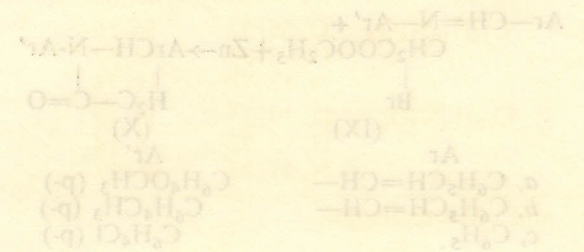
A more reasonable explanation of the preference of route (a) is that $\text{C}=\text{N}$ is less reactive than COOEt and the reaction with $\text{C}=\text{N}$ is reversible.

The ir spectrum of (VI) revealed $\nu_{\text{C}=\text{N}}$ at 2220 cm^{-1} , and $\nu_{\text{C}=\text{O}}$ at 1640 cm^{-1} .

The ir spectrum of (VII) revealed ν_{NH} at 3450 cm^{-1} , and $\nu_{\text{C}=\text{O}}$ of ester (1690 cm^{-1}), and strong band for the ketime groups at 1640 cm^{-1} , a fact which shows that VII exists in tautomeric equilibrium (VII, A-C).

The problems of 1,3-cycloaddition addition reaction of ethyl benzoate under the condition of the Reformatsky reaction was investigated by using differently substituted anils to see the effect of substitution on the mode of addition.

Ortho-*p*-aminobenzaldehyde (IXa), *o*-aminobenzaldehyde (IXb), and *p*-chlorobenzaldehyde (IXc) undergo nucleophilic addition reaction with ethyl bromoacetate to give the corresponding 1,4-dimethyl-2-aminobenzaldehyde (IXa-c).



In the present investigation the present investigation the 1,3-dipolar addition of aromatic hydrazonate derivatives to aldehydes under the condition of the Friedel-Crafts reaction was discovered. Anisalazine (I) reacts with benzene in the presence of anhydrous AlCl_3 to give three products: namely (i) anisalazine-1,3-diphenyl methyl hydrazonate (II) via addition of one mole of benzene; (ii) symmetric di-*p*-anisyl-phenyl-dimethylhydrazonate (III) via addition of two moles of benzene; (iii) asymmetric *p*-anisyl-phenyl-methylhydrazonate (IV) via addition of one mole of benzene and deacylation of one of the acylidene groups.

