

Ring Opening Of Some Furan Derivatives By Nucleophiles

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[Received 28th November, 1985, revised 13th May, 1986]

Summary: α -3-Arylidene-5-[2'-(p-cymyl)]-spirofuran-3(2H)-2-ones (Ia-d) were reacted with primary amines and gave cinnamamide derivatives (IVa-h) which were cyclized by the action of acetic anhydride and yielded the desired pyrrolin-5-ones (Va-h), also (Ia,b) were reacted with aromatic amines and anthranilic acid, the products pyrrolin-5-one derivatives (Vi-n) were obtained.

Action of ethanolic hydrazine hydrate on (Ia-d), (II) and (IIIa,b) were investigated either at room temperature or in boiling ethanol. Sodium hydroxide was affected on (IVI-1) and gave (VIa-d) also (VII) was condensed with benzaldehyde and yielded (IX). Cyclization of (VII) and (X) were investigated.

All the structures of the adducts were confirmed via either analytical data or spectroscopic possible tools.

In continuation of the previous studies [1,2] on the synthesis and reactivity of furanones, we carried out the studies on α -3-arylidene-5[2'-(p-cymyl)]-spirofuran-3(2H)-2-one derivatives (I), 5[2-(p-cymyl)]-piro [furan-3(2H)-2'-inden]-1',2',3'-trione (II), 3-{2-oxo-5-[2'-(p-cymyl)]-2,3-dihydrofurylidene}-phthalide (IIIa) and 3-{2'-oxo-5'-[2''-(p-cymyl)]-2',3'-dihydro-furylidene}-1-isoindolinone (IIIb).

The action of primary amines namely methylamine, ethylamine, and/or benzylamine on (Ia,c,d) in either boiling, ethanol or n-butanol gave α -(2'-methyl-5'-isophenyl phenacyl)-N-substituted cinnamamides (IVa-h) respectively.

Cyclization of compound (IV) was affected by the action of acetic anhydride and gave 4-arylidene 1-alkyl-2-[2'-(p-cymyl)]- Δ^2 -pyrrolin-5-ones

(Va-h) and also compounds (Va and d) could be prepared via the condensation of β -(p-cymoyl)propionic acid with aromatic aldehydes and methylamine in the presence of acetic acid-sodium acetate mixture.

Compounds (Ia and b) were reacted with aromatic amines namely aniline, p-toluidine and/or amino acid "anthranilic acid" at 165-170°C, yielded the desired 4-arylidene-1-aryl-2-[2'-(p-cymyl)]- Δ^2 -pyrrolin-5-one derivatives (Vi-n).

Arylidene spirofuranone derivatives (Ia-d) were reacted with ethanolic hydrazine hydrate at room temperature and yielded α -(2'-methyl-5'-isopropyl phenacyl)-cinnamic acid hydrazides (IVI-1) respectively.

On the other hand (Ia-d) were reacted with boiling ethanolic hydrazine hydrate and gave 4-arylidene-

2,3,4,5-tetrahydro-6-[2'-(p-cymyl)]-pyridazin-3-ones (VIa-d) respectively.

Conversion of the hydrazide derivatives (IVi-1) to the pyridazinones (VIa-d) can be affected by the action of sodium hydroxide [3].

It was observed that 5-[2''-(p-cymyl)]spiro[furan-3-3(2H)-2'-inden]-1',2',3'-trione (II) was reacted with hydrazine hydrate at room temperature and gave 2-(2'-methyl-5'-iso-propyl phenacyl)-1,3-dioxindane-2-carboxylic acid hydrazide-1,3-dihydrazone (VII), while when the reaction carried out in boiling ethanol, the product 6'-[2''-(p-cymyl)]-2',3'-dihydro-spiro[indan-2,4'(3H)-pyridazine]-1,3,3'-trione-1,3-dihydrazone (VIII) was obtained.

Condensation of (VII) with benzaldehyde gave 2-2'-methyl-5'-isopropyl phenacyl)-1,3-dioxindane-2-carboxylic acid benzylidene hydrazide-1,3-dihydrazone (IX).

However, cyclization of (VII) in boiling ethanol was carried out and gave (VIII).

Similarly 3-,2-oxo-5-[2'-(p-cymyl)-2,3-dihydrofurylidene] phthalide (IIIa) was reacted with hydrazine hydrate in ethanol at room temperature and gave 2-hydrazino carbonyl- α -(2'-methyl-5'-isopropyl phenacyl) hydrocinnamic acid hydrazide(X), while if the reaction carried out in boiling ethanol, the product 4-{4'-[6'-(2''-(p-cymyl)]-3'-oxo-2',3',4',5'-tetrahydro-pyridazinyl]}-1,2-dihydrophthalazin-1-one (XI) was obtained. The acid hydrazide (X) underwent cyclization in boiling ethanol and gave (XI) showing that (X) is probably an intermediate in the above reaction.

Reaction of 3-{2'-oxo-5'-[2''-(p-cymyl)]-2,3'-dihydro-furylidene}-1-

isoindolinone (IIIb) with hydrazine hydrate gave 3-,4'-[6'-(2''-(p-cymyl)]-3'-oxo-2',3',4',5'-tetrahydro-pyridazinylidene}, } isoindoline-1-one (XII).

All the structures of the products were confirmed by microanalysis and possible IR and PMR spectral data [4,5]. Results are listed on tables 1 and 2.

Experimental

All the melting points are uncorrected and infrared absorption spectra were determined with a Perkin Elmer spectrophotometer Model 577 using KBr pellet technique, while PMR spectra were determined with a Varian N1009 (S-60T) instrument and TMS used as internal standard.

Reaction of (Ia-d) with primary amines: Formation of (IVa-h).

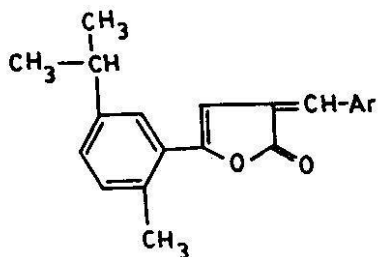
A solution of (Ia,c & d) (0.01 mole) and primary amines namely methyl, ethyl and benzylamine (0.03 mole) in 30 ml ethanol was refluxed for 6 hours. The solid products were crystallized from the proper solvent and gave pale yellow crystals (IVa-h) respectively (yield 62-70%).

Action of acetic anhydride on (IVa-h): Formation of (Va-h).

A solution of (IVa-h) (1 g) in acetic anhydride (30 ml) was heated on a steam-bath for 4 hours and poured into ice. The solids that separated were filtered off and crystallized from the suitable solvent and gave (Va-h) as yellow crystals respectively (yield 50-58%).

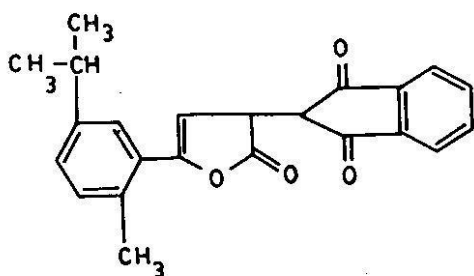
Independent synthesis of (Va and d).

A mixture of β -(p-cymoyl) propionic acid (0.01 mole), aromatic aldehydes namely benzaldehyde or p-tolu-

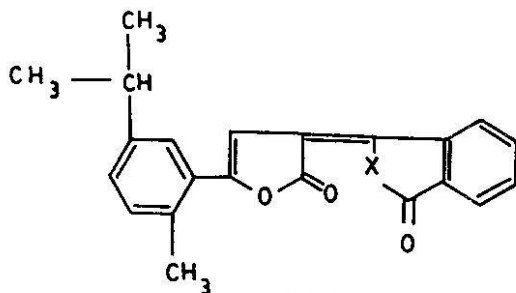


(I)

- a) Ar=C₆H₅
 b) Ar=C₆H₄-O-CH₃-p
 c) Ar=C₆H₄-CH₃-p
 d) Ar=C₆H₃-O₂-CH₂-3,4

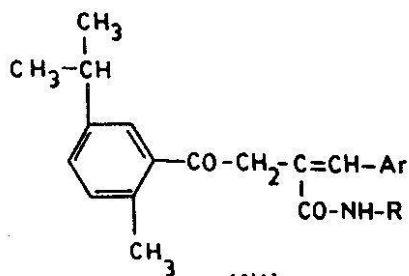


(II)



(III)

- a) X = O
 b) X = NH



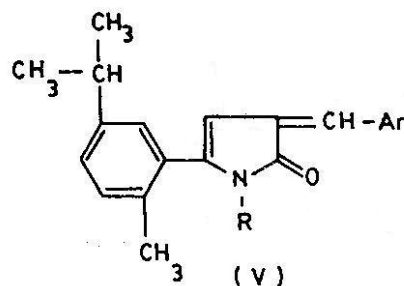
(IV)

Ar

- a) C₆H₅
 b) C₆H₅
 c) C₆H₅
 d) C₆H₅-CH₃-p
 e) C₆H₄-CH₃-p
 f) C₆H₄-CH₃-p
 g) C₆H₃O₂CH₂-3,4
 h) C₆H₃O₂CH₂-3,4
 i) C₆H₅
 j) C₆H₄-O-CH₃-p
 k) C₆H₄-CH₃-p
 l) C₆H₃-O₂CH₂-3,4

R

- CH₃
 CH₂-CH₃
 CH₂-C₆H₅
 CH₃
 CH₂-CH₃
 CH₂-C₆H₅
 CH₂-CH₃
 CH₂-C₆H₅
 NH₂
 NH₂
 NH₂
 NH₂



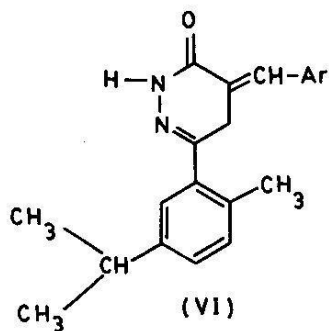
(V)

Ar

- a) C₆H₅
 b) C₆H₅
 c) C₆H₅
 d) C₆H₄-CH₃-p
 e) C₆H₄-CH₃-p
 f) C₆H₄-CH₃-p
 g) C₆H₃O₂CH₂-3,4
 h) C₆H₃O₂CH₂-3,4
 i) C₆H₅
 j) C₆H₅
 k) C₆H₅
 l) C₆H₄-OCH₃-p
 m) C₆H₄-OCH₃-p
 n) C₆H₄-OCH₃-p

R

- CH₃
 CH₂CH₃
 CH₂-C₆H₅
 CH₃
 CH₂CH₃
 CH₂-C₆H₅
 CH₂-CH₃
 CH₂-C₆H₅
 C₆H₅
 C₆H₄-CH₃-p
 C₆H₄-COOH-o
 C₆H₅
 C₆H₄-CH₃-p
 C₆H₄-COOH-o



- a) Ar = C₆H₅
 b) Ar = C₆H₄-OCH₃-p
 c) Ar = C₆H₄-CH₃-p
 d) Ar = C₆H₃-O₂CH₂-3,4

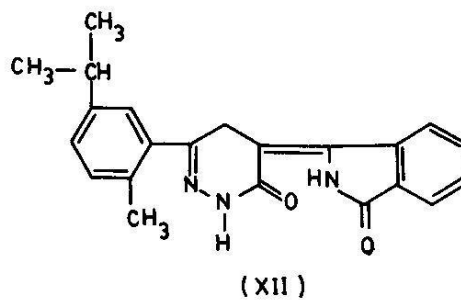
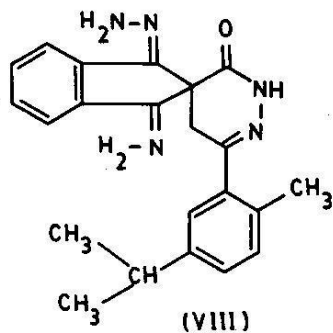
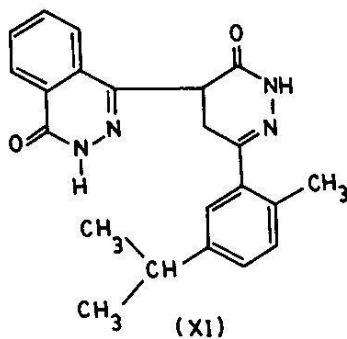
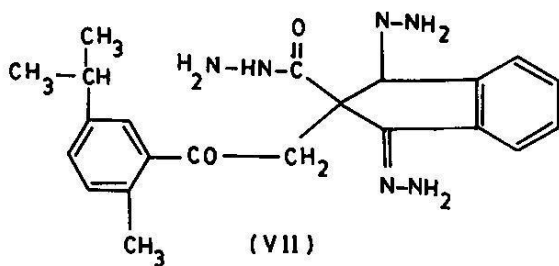
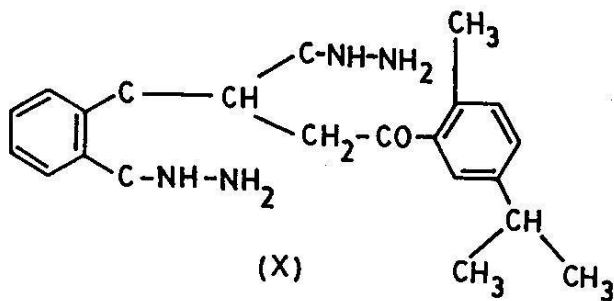
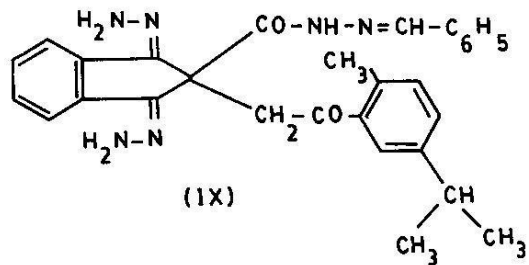


Table-1: Physical and IR data of prepared compounds

Compound	Solvent of crystn.	M.F. M.Wt	Analysis %			IR data in cm^{-1}	
			Required	Found			
			C	H	N		
(IVa)	139-40	B	$\text{C}_{22}\text{H}_{25}\text{NO}_2$ (335)	78.80	7.46	4.18	$\nu\text{C}=\text{C}$ at 1610;
				78.31	7.50	4.22	$\nu\text{C}=\text{O}$ at 1660, 1690; νCH_2 at 2940 and νNH at 3260.
(IVb)	152-153	E	$\text{C}_{23}\text{H}_{27}\text{NO}_2$ (349)	79.08	7.74	4.01	$\nu\text{C}=\text{C}$ at 1600,
				79.26	7.83	4.05	$\nu\text{C}=\text{O}$ at 1650, 1690, νCH_2 at 2980 and νNH at 3270.
(IVc)	220-21	M	$\text{C}_{28}\text{H}_{29}\text{NO}_2$ (411)	81.75	7.06	3.41	----
				81.98	7.16	3.45	
(IVd)	182-83	B	$\text{C}_{23}\text{H}_{27}\text{NO}_2$ (349)	79.08	7.74	4.01	----
				79.40	7.70	4.08	
(IVe)	159-60	B	$\text{C}_{24}\text{H}_{29}\text{NO}_2$ (363)	79.34	7.99	3.86	$\nu\text{C}=\text{C}$ at 1605,
				79.56	7.80	3.91	$\nu\text{C}=\text{O}$ at 1660, 1680, νCH_2 at 2880 and νNH at 3220.
(IVf)	238-39	B	$\text{C}_{29}\text{H}_{31}\text{NO}_2$ (425)	81.88	7.29	3.29	----
				81.61	7.36	3.24	
(IVg)	189-90	E	$\text{C}_{24}\text{H}_{27}\text{NO}_4$ (393)	73.28	6.87	3.56	$\nu\text{C}=\text{C}$ at 1610,
				73.52	6.85	3.60	$\nu\text{C}=\text{O}$ at 1650, 1695, νCH_2 at 2910 and νNH at 3260.
(IVh)	252-53	E	$\text{C}_{29}\text{H}_{29}\text{NO}_4$ (455)	76.48	6.37	3.08	----
				76.11	6.54	3.10	
(IVi)	154-55	E	$\text{C}_{21}\text{H}_{24}\text{NO}_2$ (336)	75.00	7.14	8.33	$\nu\text{C}=\text{C}$ at 1605,
				75.31	7.18	8.28	$\nu\text{C}=\text{O}$ at 1660, 1685, νCH_2 at 2890 and νNH at 3220, 3340

Table-1: (cont'd...)

Compound	Solvent of crystn.	M.F. M.Wt	Analysis %			IR data in cm^{-1}	
			Required/Found				
			C	H	N		
(IVj)	146-47	E	$\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_3$ (366)	72.13	7.10	7.65	$\nu\text{C}=\text{C}$ at 1610, $\nu\text{C}=\text{O}$ at 1650, 1690, νCH_2 at 2910 and νNH at 3220, 3310 (br)
				72.00	7.19	7.70	
(IVk)	206-207	E	$\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2$ (350)	75.43	7.43	8.00	$\nu\text{C}=\text{C}$ at 1605, $\nu\text{C}=\text{O}$ at 1655, 1690, νCH_2 at 2940 and νNH at 3180, 3320 (br)
				75.22	7.40	8.11	
(IVl)	210-11	E	$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_4$ (380)	69.47	6.32	7.37	----
(Va)	178-79	B+E	$\text{C}_{22}\text{H}_{23}\text{NO}$ (317)	83.28	7.26	4.42	$\nu\text{C}=\text{C}$ at 1610, 1630, $\nu\text{C}=\text{O}$ at 1720 and νCH at 2880
				83.99	7.20	4.51	
(Vb)	220-21	B+E	$\text{C}_{23}\text{H}_{25}\text{NO}$ (331)	83.38	7.55	4.23	$\nu\text{C}=\text{C}$ at 1600, 1620, $\nu\text{C}=\text{O}$ at 1720 and νCH at 2890
				83.81	7.50	4.25	
(Vc)	177-78	B	$\text{C}_{28}\text{H}_{27}\text{NO}$ (393)	85.50	6.87	3.56	----
(Vd)	132-33	B+E	$\text{C}_{23}\text{H}_{25}\text{NO}$ (331)	83.38	7.55	4.23	----
				82.94	7.60	4.20	
(Ve)	192-93	T	$\text{C}_{24}\text{H}_{27}\text{NO}$ (345)	83.48	7.83	4.06	$\nu\text{C}=\text{C}$ at 1605, 1620, $\nu\text{C}=\text{O}$ at 1720 and νCH at 2895
				83.62	7.80	4.10	
(Vf)	205-206	B	$\text{C}_{29}\text{H}_{29}\text{NO}$ (407)	85.50	7.13	3.44	$\nu\text{C}=\text{C}$ at 1610, 1625, $\nu\text{C}=\text{O}$ at 1725 and νCH at 2890
				85.81	7.16	3.41	
(Vg)	197-98	E	$\text{C}_{24}\text{H}_{25}\text{NO}_3$ (375)	76.80	6.67	3.73	----
				76.53	6.84	3.70	

Table-1: (continued)

Compound	Solvent	M.F.	M.Wt	Analysis %			IR data in cm^{-1}
				Required/Found			
				C	H	N	
(Vh)	188-89	E	$\text{C}_{29}\text{H}_{27}\text{NO}_3$ (437)	79.63	6.18	3.20	----
				79.28	6.24	3.11	
(Vi)	213-214	Ac	$\text{C}_{27}\text{H}_{25}\text{NO}$ (379)	85.49	6.60	3.69	----
				85.72	6.54	3.73	
(Vj)	261-62	Ac	$\text{C}_{28}\text{H}_{27}\text{NO}$ (393)	85.50	6.87	3.56	$\nu\text{C}=\text{C}$ at 1610, 1625,
				85.74	6.80	3.60	$\nu\text{C}=\text{O}$ at 1725 and νCH at 2910
(Vk)	> 300	Ac	$\text{C}_{28}\text{H}_{25}\text{NO}_3$ (423)	79.43	5.91	3.31	$\nu\text{C}=\text{C}$ at 1610, 1630,
				79.65	5.88	3.36	$\nu\text{C}=\text{O}$ at 1710, 1740 and νOH of acid at 3460 (br)
(Vl)	258-59	Ac	$\text{C}_{28}\text{H}_{27}\text{NO}_2$ (409)	82.15	6.60	3.42	$\nu\text{C}=\text{C}$ at 1600, 1620,
				82.00	6.55	3.52	$\nu\text{C}=\text{O}$ at 1715 and νCH at 2885
(Vm)	277-78	EA	$\text{C}_{29}\text{H}_{29}\text{NO}_2$ (423)	82.27	6.86	3.31	----
				81.94	6.77	3.45	
(Vn)	> 300	EA+Ac	$\text{C}_{29}\text{H}_{27}\text{NO}_4$ (453)	76.52	5.96	3.09	$\nu\text{C}=\text{C}$ at 1610, 1625,
				77.04	5.82	3.16	$\nu\text{C}=\text{O}$ at 1710, 1730, and νOH (acid) at 3450 (br)
(VIa)	180-81	B	$\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}$ (318)	79.24	6.92	8.80	$\nu\text{C}=\text{C}$ at 1610,
				79.42	6.95	8.62	$\nu\text{C}=\text{N}$ at 1630, $\nu\text{C}=\text{O}$ at 1660 and νNH at 3240
(VIb)	207-208 (decompn)	B	$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2$ (348)	75.86	6.90	8.04	----
				75.54	6.88	8.14	
(VIc)	161-62	B	$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}$ (332)	79.50	7.23	8.43	$\nu\text{C}=\text{C}$ at 1610,
				79.80	7.18	8.48	$\nu\text{C}=\text{N}$ at 1640, $\nu\text{C}=\text{O}$ at 1655 and νNH at 3260

Table-1: (cont'd..)

Compound	Solvent	M.F.	Analysis %			IR data in cm^{-1}		
			of crystn.	M.Wt	Required/Found			
					C		H	N
(VIId)	142-43 (decompn)	X	$\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_3$	72.93	6.08	7.73	----	
			(362)	72.69	6.12	7.90		
(VII)	219-20	E	$\text{C}_{22}\text{H}_{26}\text{N}_6\text{O}_2$	65.02	6.40	20.69	$\nu\text{C}=\text{N}$ at 1630, $\nu\text{C}=\text{O}$ at 1660, 1680 and νNH at 3210, 3280 (br)	
			(406)	64.94	6.44	20.90		
(VIII)	>300	M	$\text{C}_{22}\text{H}_{24}\text{N}_6\text{O}$	68.04	6.19	21.65	$\nu\text{C}=\text{N}$ at 1625, $\nu\text{C}=\text{O}$ at 1670 and νNH at 3240, 3310 (br)	
			(388)	68.31	6.21	21.89		
(IX)	179-80	B	$\text{C}_{29}\text{H}_{30}\text{N}_6\text{O}_2$	70.45	6.07	17.00	$\nu\text{C}=\text{C}$ at 1610, $\nu\text{C}=\text{N}$ at 1630, $\nu\text{C}=\text{O}$ at 1650, 1670 and νNH at 3210, 3290 (br)	
			(494)	70.69	6.03	17.23		
(X)	166-67	E	$\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_4$	64.39	6.34	13.66	$\nu\text{C}=\text{N}$ at 1630, $\nu\text{C}=\text{O}$ at 1665, 1680 and νNH at 3190, 3280 (br)	
			(410)	64.21	6.16	13.80		
(XI)	138-39	E+B	$\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_2$	70.59	5.88	14.97	$\nu\text{C}=\text{N}$ at 1620, $\nu\text{C}=\text{O}$ at 1680 and νNH at 3180 (br)	
			(374)	70.30	5.92	14.00		
(XII)	217-218	Ac	$\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}$	76.97	6.12	12.24	$\nu\text{C}=\text{C}$ at 1600, $\nu\text{C}=\text{O}$ at 1670, 1690 and νNH at 3240, 3320 (br)	
			(343)	76.79	6.10	12.28		

B = Benzene, E = Ethanol, M = Methanol, Ac = Acetic acid, X = Xylene
and EA = Ethyl acetate.

Table-2: PMR Spectra of Some New Compounds

Compound	Solvent	values	No. of protons	Group
(IVa)	CDCl ₃	<u>s</u> , 1.30	<u>6H</u>	<u>CH₃-CH-CH₃</u>
		<u>s</u> , 2.41	<u>3H</u>	Ar- <u>CH₃</u>
		<u>s</u> , 2.86	<u>2H</u>	Ar-CO- <u>CH₂-</u>
		<u>m</u> , 2.98	<u>1H</u>	Ar- <u>CH-</u>
		<u>d</u> , 3.05	<u>3H</u>	-CO-N- <u>CH₃</u>
		<u>br</u> , 5.37	<u>1H</u>	-CO-NH-
		<u>s</u> , 5.65	<u>1H</u>	Ar- <u>CH=C-</u>
		<u>m</u> , 7.33-7.61	<u>8H</u>	<u>Ar-protons</u>
(IVf)	(CD ₃) ₂ CO	<u>s</u> , 1.32	<u>6H</u>	<u>CH -CH-CH₃</u>
		<u>s</u> , 2.64	<u>6H</u>	two Ar- <u>CH₃</u>
		<u>s</u> , 2.92	<u>2H</u>	-CO- <u>CH₂-</u>
		<u>m</u> , 3.04	<u>1H</u>	Ar- <u>CH-</u>
		<u>d</u> , 4.15	<u>2H</u>	Ar- <u>CH₂-N-</u>
		<u>br</u> , 5.18-5.24	<u>1H</u>	-CO- <u>NH-</u>
		<u>s</u> , 5.57	<u>1H</u>	Ar- <u>CH=C-</u>
		<u>m</u> , 7.24-7.58	<u>12H</u>	<u>Ar-protons</u>
(IVi)	(CD ₃) ₂ CO	<u>s</u> , 1.36	<u>6H</u>	<u>CH₃-CH-CH₃</u>
		<u>s</u> , 2.48	<u>3H</u>	Ar- <u>CH₃</u>
		<u>s</u> , 2.84	<u>2H</u>	Ar-CO- <u>CH₂-</u>
		<u>m</u> , 3.01	<u>1H</u>	Ar- <u>CH-</u>
		<u>s</u> , 5.61	<u>1H</u>	Ar- <u>CH=C-</u>
		<u>br</u> , 5.68-5.76	<u>2H</u>	-CO-N- <u>NH₂</u>
		<u>br</u> , 6.72-6.82	<u>1H</u>	-CO- <u>NH-N-</u>
		<u>m</u> , 7.31-7.54	<u>8H</u>	<u>Ar-protons</u>
(IVl)	CDCl ₃	<u>s</u> , 1.28	<u>6H</u>	<u>CH₃-CH-CH₃</u>
		<u>s</u> , 2.44	<u>3H</u>	Ar- <u>CH₃</u>
		<u>s</u> , 2.93	<u>2H</u>	Ar-CO- <u>CH₂-</u>
		<u>m</u> , 3.04	<u>1H</u>	Ar- <u>CH-</u>
		<u>s</u> , 5.65	<u>1H</u>	Ar- <u>CH=C-</u>
		<u>br</u> , 5.64-5.78	<u>2H</u>	-CO-N- <u>NH₂</u>

Table-2: (cont'd..)

Compound	Solvent	values	No. of protons	Group		
(Va)	CDCl ₃	<u>s</u> , 5.93	<u>2H</u>	-C ₆ H ₃ -O ₂ -CH ₂ ,3,4-		
		<u>br</u> , 6.61-6.74	<u>1H</u>	-CO-NH-N-		
		<u>m</u> , 7.24-7.53	<u>6H</u>	Ar-protons		
		<u>s</u> , 1.32	<u>6H</u>	CH ₃ -CH-CH ₃		
		<u>s</u> , 2.41	<u>3H</u>	Ar-CH ₃		
		<u>m</u> , 2.94	<u>1H</u>	Ar-CH-		
		<u>s</u> , 3.11	<u>3H</u>	-N-CH ₃		
		<u>s</u> , 6.08	<u>1H</u>	Ar-C=C-CH=C		
		<u>s</u> , 6.56	<u>1H</u>	Ar-CH=C-		
(VIb)	CDCl ₃	<u>m</u> , 7.32-7.58	<u>8H</u>	Ar-protons		
		<u>s</u> , 1.28	<u>6H</u>	CH ₃ -CH-CH ₃		
		<u>s</u> , 2.44	<u>3H</u>	Ar-CH ₃		
		<u>m</u> , 3.04	<u>1H</u>	Ar-CH-		
		<u>s</u> , 3.22	<u>2H</u>	-CH ₂ -		
		<u>s</u> , 3.88	<u>3H</u>	Ar-OCH ₃		
		<u>br</u> , 5.66-5.88	<u>1H</u>	-CO-NH-		
		<u>s</u> , 6.18	<u>1H</u>	Ar-CH=C-		
		<u>m</u> , 7.24-7.48	<u>7H</u>	Ar-protons		
(VII)	(CD ₃) ₂ CO ₃	<u>s</u> , 1.34	<u>6H</u>	CH ₃ -CH-CH ₃		
		<u>s</u> , 2.48	<u>3H</u>	Ar-CH ₃		
		<u>s</u> , 2.91	<u>2H</u>	Ar-CO-CH ₂ -		
		<u>m</u> , 3.02	<u>1H</u>	Ar-CH-		
		<u>br</u> , 5.48-5.54	<u>6H</u>	three-N-NH ₂		
		<u>br</u> , 6.48-6.56	<u>1H</u>	-N-NH-CO-		
		<u>m</u> , 7.28-7.52	<u>7H</u>	Ar-protons		
		(VIII)	CDCl ₃	<u>s</u> , 1.33	<u>6H</u>	CH ₃ -CH-CH ₃
				<u>s</u> , 2.46	<u>3H</u>	Ar-CH ₃
<u>m</u> , 3.08	<u>1H</u>			Ar-CH-		
<u>s</u> , 3.26	<u>2H</u>			-CH ₂ -		
<u>br</u> , 5.38-5.52	<u>4H</u>			two H ₂ N-N-		
<u>br</u> , 5.74-5.80	<u>1H</u>			-CO-NH-		
<u>m</u> , 7.31-7.57	<u>7H</u>			Ar-protons		

Table-2: (cont'd..)

Compound	Solvent	values	No. of protons	Group
(IX)	$(\text{CD}_3)_2\text{CO}$	<u>s</u> , 1.28	<u>6H</u>	$\text{CH}_3\text{-CH-CH}_3$
		<u>s</u> , 2.51	<u>3H</u>	Ar-CH_3
		<u>s</u> , 2.92	<u>2H</u>	$\text{Ar-CO-CH}_2\text{-}$
		<u>m</u> , 3.04	<u>1H</u>	Ar-CH-
		<u>br</u> , 5.32-5.48	<u>4H</u>	two $\text{H}_2\text{-N-N-}$
		<u>br</u> , 5.83-5.91	<u>1H</u>	CO-NH-N
		<u>m</u> , 7.24-7.48	<u>12H</u>	Ar-protons
		<u>s</u> , 7.66	<u>1H</u>	Ar-CH=N-N
(X)	CDCl_3	<u>s</u> , 1.27	<u>6H</u>	$\text{CH}_3\text{-CH-CH}_3$
		<u>s</u> , 2.42	<u>3H</u>	Ar-CH_3
		<u>d</u> , 2.96	<u>2H</u>	$\text{Ar-CO-CH}_2\text{-}$
		<u>m</u> , 3.06	<u>1H</u>	Ar-CH-
		<u>t</u> , 4.18	<u>1H</u>	Ar-CO-CH-CO-
		<u>br</u> , 5.34-5.51	<u>4H</u>	two $\text{H}_2\text{-N-N-}$
		<u>br</u> , 5.72-5.88	<u>2H</u>	two CO-NH-N-
		<u>m</u> , 7.28-7.62	<u>7H</u>	Ar-protons
(XI)	CDCl_3	<u>s</u> , 1.28	<u>6H</u>	$\text{CH}_3\text{-CH-CH}_3$
		<u>s</u> , 2.62	<u>3H</u>	Ar-CH_3
		<u>m</u> , 3.04	<u>1H</u>	Ar-CH-
		<u>d</u> , 3.11	<u>2H</u>	$\text{-CH}_2\text{-}$
		<u>t</u> , 4.28	<u>1H</u>	-CH-C=O
		<u>br</u> , 5.69-5.81	<u>2H</u>	two -C- NH-
		<u>m</u> , 7.28-7.63	<u>7H</u>	Ar-protons
		<u>s</u> , 1.34	<u>6H</u>	$\text{CH}_3\text{-CH-CH}_3$
(XII)	$(\text{CD}_3)_2\text{CO}$	<u>s</u> , 2.58	<u>3H</u>	Ar-CH_3
		<u>m</u> , 2.96	<u>1H</u>	Ar-CH-
		<u>s</u> , 3.18	<u>2H</u>	$\text{-CH}_2\text{-}$
		<u>br</u> , 5.54-5.78	<u>2H</u>	two -CO-NH-
		<u>m</u> , 7.34-7.63	<u>7H</u>	Ar-protons

aldehyde (0.01 mole), methylamine (0.015 mole), freshly fused sodium acetate (0.02 mole) and 30 ml Ac_2O were heated under reflux for 6 hours, the solid products were filtered off and crystallized from the proper solvent and yielded (Va and d) respectively as yellow crystals which were identified by m.p., mixed m.p. and comparison of their IR data (yield 33-41 %).

Action of aromatic amines and amino acid on (Ia and b): Formation of (Vi-n).

Method (A):

A mixture of (Ia and b) (0.01 mole), aromatic amine namely aniline and p-toluidine or anthranilic acid (0.015 mole), acetic anhydride (10 ml) and freshly prepared sodium acetate (0.02 mole) were refluxed for 24 hours and the reaction mixture was poured into ice-cold water. The solid products were crystallized from the proper solvent and (Vi-n) were obtained respectively as yellow crystals and yield (45-52 %).

Method (B):

A mixture of (Ia and b) (0.01 mole), and aniline, p-toluidine or anthranilic acid (0.015 mole) was heated at 165-170°C for 10 hours in an oil bath. The solid products were crystallized from the suitable solvent and gave yellow crystals (Vi-n) respectively (yield 60-68 %).

Reaction of (Ia-d), (II) and (IIIa) with hydrazine hydrate in ethanol at room temperature: Formation of (IVi-L), (VII) and (X).

A solution of (Ia-d), (II) and (IIIa) (0.01 mole) and hydrazine hydrate (0.05 mole) in ethanol (30 ml) was left at room temperature for 24

hours. The solid products were crystallized from the suitable solvent and gave (IVi-L), (VII) and (X) respectively as pale yellow crystals (yield 58-65 %).

Reaction of (Ia-d), (II) and (IIIa,b) with hydrazine hydrate in boiling ethanol: Formation of (VIa-d), (VIII), (XI) and (XII).

A solution of (Ia-d), (II), (IIIa and b) (0.01 mole) and hydrazine hydrate (0.03 mole) in ethanol (50 ml) was refluxed for 6 hours, and the solution concentrated. The solid products obtained were crystallized from the proper solvent and gave (VIa-d), (VII), (XI) and (XII) respectively as yellow crystals (yield 44-56 %).

Action of sodium hydroxide on (IVi-L): Formation of (VIa-d).

A solution of (IVi-L) (0.01 mole) in 10% sodium hydroxide (35 ml) was refluxed for 6 hours. The reaction mixture was acidified with dil. HCl and the solid products were crystallized from the suitable solvent and yielded (VIa-d) respectively as yellow crystals (yield 38-42 %).

Independent synthesis of (XII).

A mixture of β -(p-cymoyl)-propionic acid (0.01 mole), phthalimide (0.01 mole), freshly fused sodium acetate (0.02 mole) acetic anhydride (30 ml) and hydrazine hydrate (0.015 mole) was refluxed for 6 hours and the reaction mixture was poured into ice-water, the solid product that obtained was crystallized from acetic acid and yielded (XII) as yellow crystals which was identified by m.p., mixed m.p. and comparison of IR data, (yield 45 %).

Condensation of (VIII) with benzaldehyde: Formation of (IX).

A solution of (VII) (0.01 mole) in ethanol (30 ml) was treated with benzaldehyde (0.01 mole), and the reaction mixture was refluxed for 8 hours. The excess solvent was removed and the solid product was crystallized from benzene and gave (IX) as pale yellow crystals (yield 56 %).

Cyclization of (VII), (X): Formation of (VIII) and (XI).

A solution of (VII) or (X) (1 g) in 30 ml ethanol was refluxed for 12 hours. The excess of solvent, was evaporated, and the solid product was crystallized from the proper solvent

and gave (VIII) and (XI) respectively as yellow crystals (yield 38-46 %).

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