

## **SYNTHESIS & RING OPENING REACTION OF SUBSTITUTED 2, 3, 8, 9-TETRAAZADISPIRO [4.0.4.1] UNDECA-1, 9-DIENES**

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11 – Aryl – 1, 10-dimethyl-4, 7 – dioxo – 3, 8 – diphenyl-  
(IIa-m) – and 11-aryl-1, 10-methyl-4, 7-dioxo(IIa-n)-2, 3, 8,  
9-tetraazadispiro [4.0.4.1] undeca-1, 9-dienes have been  
prepared by two different routes. Hydrolysis of II with  
ethanolic HCl or acetic acid brings about opening of the  
bond between the two spiro carbons of the cyclopropane  
ring to give compounds Va-y containing a hydroxyl group.  
All the compounds have been screened for their antifungal  
activity.

### **INTRODUCTION**

**T**wo methods have been used for the synthesis of the substituted 2, 3, 8, 9-tetraazadispiro [4.0.4.1] undeca-1, 9- dienes (IIa-y) (Table 1). In the first method, appropriate arylidene-4, 4'-bis (1-aryl-3-methyl-2-pyrazolin-5-ones) (I) [1] dissolved in NaOH were treated with a satd. solution of iodine in KI to give the desired spiro compounds (II). The second process, which is a modification of the Westoo [2] method, involved the Michael addition of 4-arylidene-2-pyrazolin-5-ones (III) [3] on appropriate 4-bromo-2-pyrazolin-5-ones (IV) [4, 5].

Structures of II were supported by their IR, NMR and mass spectral data. Their IR spectra shows bands at 3050, 1735 and 1600  $\text{cm}^{-1}$  attributable to – CH of the cyclopropane moiety, carbonyl group and aromatic moiety, respectively. The NMR ( $\text{CCl}_4$ ) spectra of II exhibited signals at  $\delta$  2.03, 2.49 and 4.26 assignable to the two – $\text{CH}_3$  groups and the –CH (benzylidene hydrogen) of cyclopropane moiety respectively.

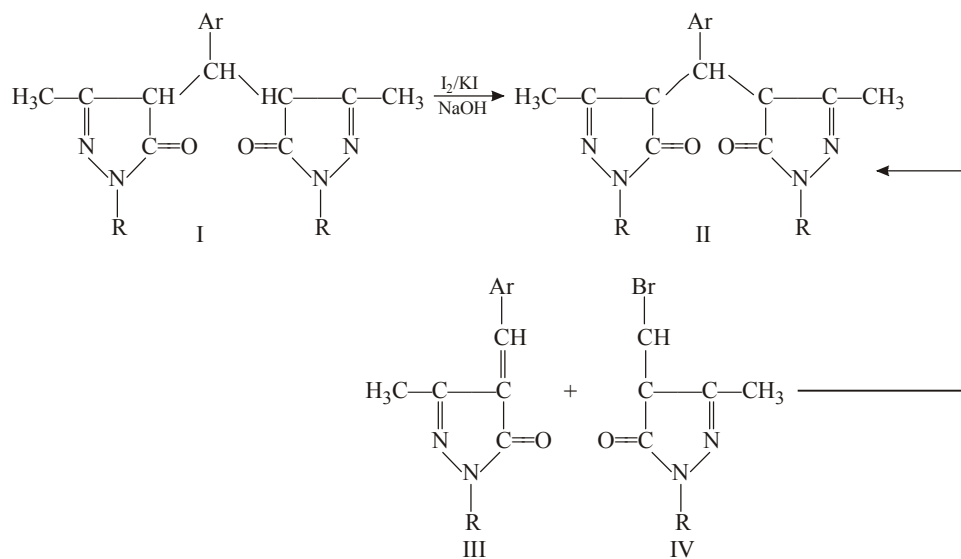
All the spiro compounds (IIa-y) when refluxed with ethanolic HCl or AcOH for 2 hr were hydrolysed to give the products (Va-y; Table 2) containing a hydroxyl group. The hydrolysis product on treatment with  $\text{POCl}_3$  followed by reaction with NaOH gave back the original respective spiro compound (II). This clearly shows that the hydrolysis of II brings about rupturing of the bond between the two spiro carbons of the cyclopropane ring. Absence of an IR band in the hydrolysed products (V) at 3100 to 2990  $\text{cm}^{-1}$  attributable to the –CH group in cyclopropane ring supported the above contention. Further a broad band at 2700-3000  $\text{cm}^{-1}$  indicated the presence of OH group in V.

*Antifungal activity* – All the spiro compounds (IIa-y) and their hydrolysis products (Va-y) were screened for their antifungal activity against the rice blast pathogen, *Pyricularia oryzae* and the brown leaf spot pathogen *Helminthosporium oryzae* by the standard method using spore germination tests at various concentrations [6]. The results are given in Table 1 and 2. The rate of germination inhibition was higher in the case of II than the hydrolysis products (V). It is, therefore, concluded that the additional toxic effect in II is due to the presence of a cyclopropane ring.

A comparison of the activities of synthesized compounds with those of standard fungicides like O-ethyl-S,S-diphenyl phosphorodithioate (Hinosan 50%) EL, Difolatan 50% WP and Derosal 60% WP which inhibit 95, 98 and 87% of spore germination respectively at 1000 ppm concentration against the pathogen *P. oryzae*, it was noted that compounds IIa, IIg, IIj, IIv, Va, Vc and Vk inhibit spore germination in the same range as the above standard fungicides. Therefore, these may be used as commercial fungicides.

*Substituted 2, 3, 8, 9-tetraazadispiro [4.0.4.1] undeca-1, 9 dienes (IIa-v); Method (i)* The appropriate arylidene – 4, 4'- bis(1-aryl-3-methyl-2-pyrazolin-5-one) (I; 5g) was dissolved in 20% NaOH solution (25 ml) at room temperature, and satu. solution of iodine in KI added to it dropwise with constant stirring for 2 hr. The yellowish precipitate obtained was filtered, washed with 20% solution thiosulphate followed by water and crystallized from acetone to give II (Table I) as yellow needles, yield 75% insoluble in 10% NaOH and gives no colouration with ethanolic FeCl<sub>3</sub>.

*Method (ii)* – To a solution of the appropriate 4-arylidene-3-methyl-2-pyrazolin-5-one (III: 2 g) in ethanol (5 ml) was added a solution of 4-bromo-3-methyl-2-pyrazolin-5-one (IV: 1.6 g) in 10% NaOH (6 ml) at room temperature. The immediately precipitated compound was filtered, washed repeatedly with water and crystallized from acetone to give yellowish needles of II (Table 1), yield 70%.



**Table 1. Physical and Fungicidal Data of 11-Aryl-1, 10- Dimethyl-4, 7-dioxo- 3, 8-diphenyl (IIa-m) and 11-aryl-1, 10-dimethyl-4.7-dioxo (II n-y)-2.3, 8,9-tetraazadispiro [4.0.4.1] undeca-1, 9-dienes**

Compd(a)	Ar	M.P. °C	Germination inhibition (%) at 1000 ppm	
			P. oryzae	H. oryzae
R = C <sub>6</sub> H <sub>5</sub>				
IIa	C <sub>6</sub> H <sub>5</sub>	162	98	75
IIb	o-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	142	85	54
IIc	m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	189	63	54
IId	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	180	65	47
IIe	o-ClC <sub>6</sub> H <sub>4</sub>	184	50	49
IIf	o-OHC <sub>6</sub> H <sub>4</sub>	170	60	65
IIg	m-OHC <sub>6</sub> H <sub>4</sub>	192	88	72
IIh	p-OHC <sub>6</sub> H <sub>4</sub>	310	75	63
IIi	2-OH-3-BrC <sub>6</sub> H <sub>3</sub>	158	75	68
IIj	2-OH-3,5-Br <sub>2</sub> C <sub>6</sub> H <sub>2</sub>	108	87	65
IIk	2-CH <sub>3</sub> O-3,5-Br <sub>2</sub> C <sub>6</sub> H <sub>2</sub>	110	69	62
III	m-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	168	33	33
IIlm	3-CH <sub>3</sub> O-4-OHC <sub>6</sub> H <sub>3</sub>	124	66	62
R = H				
II n	C <sub>6</sub> H <sub>5</sub>			
IIo	o-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>			
IIp	m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>			
IIq	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>			
IIr	m-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>			
IIs	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>			
IIt	o-OHC <sub>6</sub> H <sub>4</sub>			
IIu	m-OHC <sub>6</sub> H <sub>4</sub>			
IIv	p-OHC <sub>6</sub> H <sub>4</sub>			
IIw	2-OH-3-BrC <sub>6</sub> H <sub>3</sub>			
IIx	2-OH-3,5-Br <sub>2</sub> C <sub>6</sub> H <sub>3</sub>			
IIy	2-CH <sub>3</sub> O-3,5-Br <sub>2</sub> C <sub>6</sub> H <sub>2</sub>			

(a) All the compounds gave satisfactory C, H and N analyses.

*Hydrolysis of II : Formation of V* – The spiro compound (II; 1 g) was hydrolysed with ethanolic HCl or acetic acid (4 ml) over a water-bath for 2 hr. After removing ethanol or acetic acid, the mass was treated with distilled water (5 ml) when a light yellow compound separated out which was filtered, washed with water and crystallized from ethanol to give yellow crystals of V (Table 2), yield 80%; soluble in 10% aq. NaOH and gives colouration with ethanolic FeCl<sub>3</sub>; IR (KBr): 2810, 1595, 1500, 1410 cm<sup>-1</sup>.

Table 2 – Physical and Fungicidal Data of the Hydrolysis Products (Va-y)

Compd (a)	Ar	M.P. °C	Germination inhibition (%) at 1000 ppm	
			P. oryzae	H. oryzae
R = C <sub>6</sub> H <sub>5</sub>				
Va	C <sub>6</sub> H <sub>5</sub>	226	94	60
Vb	o-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	154	78	66
Vc	m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	127	87	65
Vd	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	228	67	60
Ve	o-ClC <sub>6</sub> H <sub>4</sub>	92	68	60
Vf	o-OHC <sub>6</sub> H <sub>4</sub>	186	61	62
Vg	m-OHC <sub>6</sub> H <sub>4</sub>	185	61	62
Vh	p-OHC <sub>6</sub> H <sub>4</sub>	307	60	62
Vi	2-OH-3-BrC <sub>6</sub> H <sub>3</sub>	172	67	63
Vj	2-OH-3,5-Br <sub>2</sub> C <sub>6</sub> H <sub>2</sub>	140	64	66
Vk	2-CH <sub>3</sub> O-3,5-Br <sub>2</sub> C <sub>6</sub> H <sub>2</sub>	104	94	65
Vl	m-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	298(d)	65	65
Vm	3-CH <sub>3</sub> O-4-OHC <sub>6</sub> H <sub>3</sub>	131	64	60
R = H				
Vn	C <sub>6</sub> H <sub>5</sub>	152	54	50
Vo	o-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	137	48	46
Vp	m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	142	69	64
Vq	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	>350	60	61
Vr	m-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	>350	70	68
Vs	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	187	65	60
Vt	o-OHC <sub>6</sub> H <sub>4</sub>	277	63	61
Vu	m-OHC <sub>6</sub> H <sub>4</sub>	212	67	64
Vv	p-OHC <sub>6</sub> H <sub>4</sub>	193	64	68
Vw	2-OH-3-BrC <sub>6</sub> H <sub>3</sub>	265	50	53
Vx	2-OH-3,5-Br <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	284	64	60
Vy	2-CH <sub>3</sub> O-3,5-Br <sub>2</sub> C <sub>6</sub> H <sub>2</sub>	214	62	60
(a) All the compounds gave satisfactory C, H and N analyses.				

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