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SYNTHESIS AND SOME REACTIONS OF 1-PHENYL-3-METHYL-2-PYRAZOLIN-5-ONE DERIVATIVES

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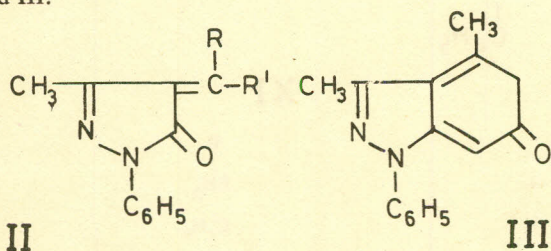
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Abstract. Chemical reactions of 2-pyrazolin-5-one derivatives with diketones, chalcones aromatic hydrocarbons, Grignard reagents, hydrazines, amines and hydroxylamine hydrochloride has been investigated.

3-Methyl-1-phenyl-5-pyrazolone was found to stimulate plant growth, increase the size and hasten the ripening of tomato, potato and vines.¹⁴ Structure-activity relationship of pyrazolinones was studied by A. Essawy *et al.*¹⁵ The aim of the present investigation is to synthesise some new 2-pyrazolin-5-one derivatives. Their phytotoxic and fungitoxic actions were studied.¹⁵ Some of these compounds were found to be antimicrobial.¹⁶

Results and Discussion

During the present investigation it was found that 1-phenyl-3-methyl-2-pyrazolin-5-one(1) underwent condensation with diketone¹⁻⁵ to give the products (II a - c) and III.

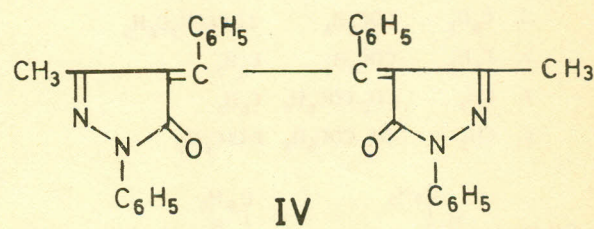


- | | | | |
|----|-----------------------------------|---|---|
| a, | R = C ₆ H ₅ | ; | R' = COC ₆ H ₅ |
| b, | R = CH ₃ | ; | R' = CH ₂ -COCH ₃ |
| c, | R = CH ₃ | ; | R' = COCH ₃ |

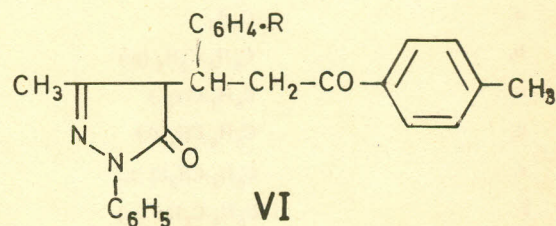
However, on using excess of pyrazolin-one (I) two moles condense with one mole of benzil to give compound (IV).^{1,5}

The Michael addition of (I) to different chalcones (Va and Vb) leads to the formation of the Michael adducts (VIa and b) respectively.^{5,6}

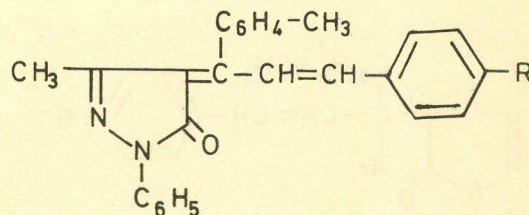
On the other hand the pyrazolin one (I) underwent Claisen Condensation with chalcones (Va and b) to give the coloured condensation products (VIIa and b).⁵ Alkylation of aromatic compounds such as anisole, cumene, chlorobenzene, *o*-chlorotoluene benzene, ethyl benzene and *m*-xylene by IIa, IIb, (IV) and (VIIa



- a, R = H
b, R = OCH₃



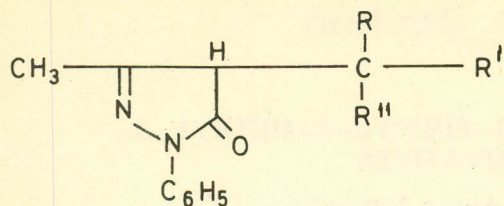
- a, R = H
b, R = OCH₃



VII

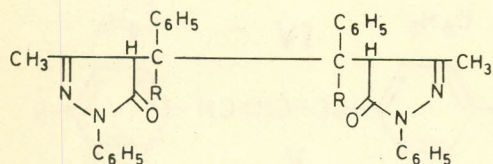
- | | | | |
|----|---|---|------------------|
| a, | R | = | H |
| b, | R | = | OCH ₃ |

and b) in the presence of AlCl₃ gave (VIII a - g) (IXa - h) and (XXI a - g) respectively via, 1,2 dipolar addition to the exocyclic double bond.^{8,9}



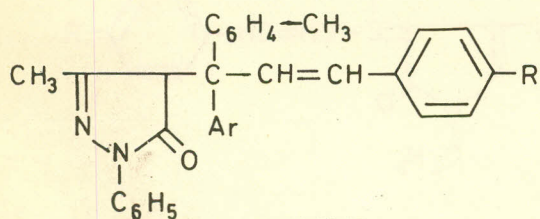
VIII

	R	R'	R''
a.	C ₆ H ₅	COC ₆ H ₅	P-CH ₃ OC ₆ H ₄
b.	C ₆ H ₅	COC ₆ H ₅	P-C ₃ H ₇ .C ₆ H ₄
c.	C ₆ H ₅	COC ₆ H ₅	P-Cl.C ₆ H ₄
d.	C ₆ H ₅	COC ₆ H ₅	2,3,Cl.CH ₃ C ₆ H ₃
e.	C ₆ H ₅	COC ₆ H ₅	C ₆ H ₅
f.	CH ₃	CH ₂ .COC ₆ H ₅	C ₆ H ₅
g.	CH ₃	CH ₂ .COC ₆ H ₅	P-Cl-C ₆ H ₄



IX

	R
a.	C ₆ H ₅
b.	C ₆ H ₄ .C ₂ H ₅ (p.)
c.	C ₆ H ₄ .Cl (p.)
d.	C ₆ H ₄ .CH ₃ (p.)
e.	C ₆ H ₃ .CH ₃ Cl 2,3
f.	C ₆ H ₄ .C ₃ H ₇ (p.)
g.	C ₆ H ₃ (CH ₃) ₂ ,2,4
h.	C ₆ H ₄ OCH ₃ (p.)



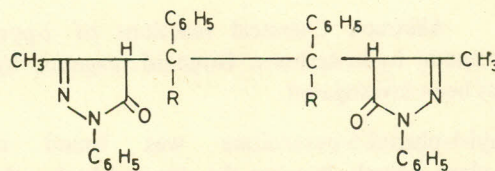
XXI

	R	Ar
a.	H	C ₆ H ₄ .CH ₃ (p)
b.	H	C ₆ H ₃ (CH ₃) ₂ 2,4
c.	H	C ₆ H ₄ .Cl (p.)
d.	OCH ₃	C ₆ H ₄ .OCH ₃ (p.)

e.	OCH ₃	C ₆ H ₄ .CH ₃ (p)
f.	OCH ₃	C ₆ H ₄ .Cl (p)
g.	OCH ₃	C ₆ H ₃ (CH ₃) ₂ 2,4

The same compounds (IXa and b) are obtained by the action of phenyl magnesium bromide and/or *p*-tolyl-magnesium iodide on compound (IV).

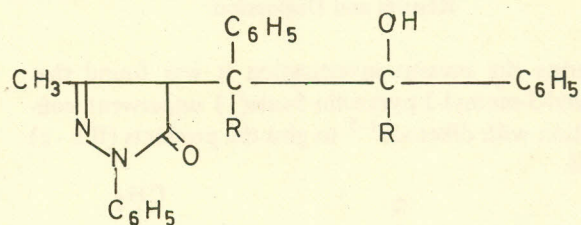
4,4-Diphenyl ethylidene-bis (1-phenyl-3-methyl-2-pyrazolin-5-one) (IV) reacts with Grignard reagents (2 moles) via addition to the double bond of the lateral chain to give (Xa-d).⁷



X

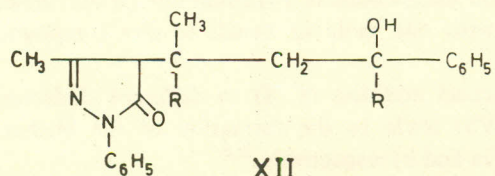
	R	R	R	R
a)	CH ₃	b) C ₂ H ₅	c) CH ₂ C ₆ H ₅	d) C ₆ H ₁₁

IIa and b reacted with Grignard reagents affording (Xla-e) and (XIIa and b)^{7,10}



XI

	R
a.	CH ₃
b.	C ₂ H ₅
c.	CH ₂ C ₆ H ₅
d.	C ₆ H ₄ .CH ₃ (O)
e.	C ₆ H ₅

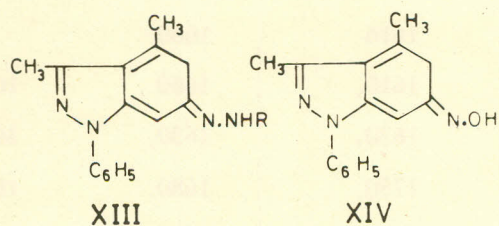


XII

	R
a.	CH ₃
b.	C ₆ H ₄ .CH ₃ (O)

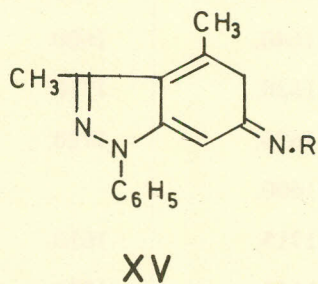
Treatment of compound III with hydrazine hydrate and/or phenyl hydrazine in boiling alcohol gave the corresponding hydrazones (XIIIa and b)^{11,12}

Treatment of III with hydroxylamine hydrochloride in boiling pyridine affected the formation of the corresponding oxime (XIV)¹²



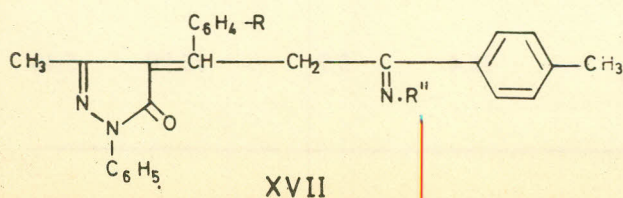
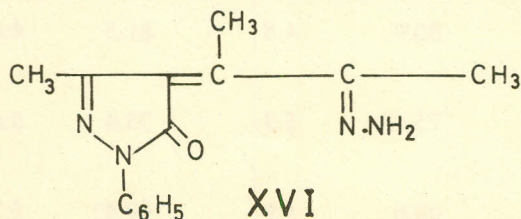
- | | R |
|----|-------------------------------|
| a. | H |
| b. | C ₆ H ₅ |

The reaction of III with benzylamine and/or methylamine in boiling alcohol (molar ratio 1:1) was found to give the cyclic product (XV)¹¹



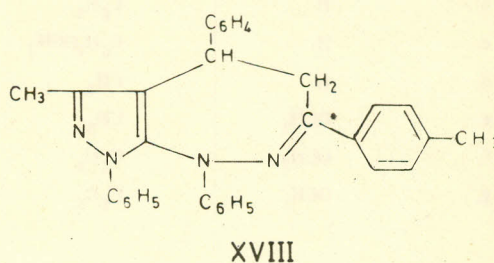
- | | |
|---|--|
| a | R = CH ₃ |
| b | R = CH ₂ -C ₆ H ₅ |

Condensation of IIIc with hydrazine hydrate in boiling alcohol yielded the hydrazone (XVI). Treatment of (VIa and b) with hydrazine, phenyl hydrazine, methyl amine and/or butylamine in boiling alcohol affected the formation of the products (XVIIa-g).



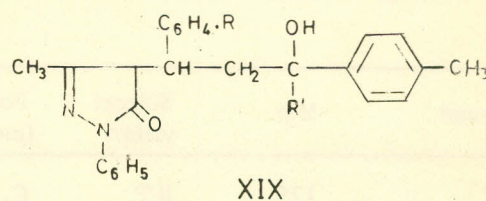
	R	R'
a.	H	NH ₂
b.	H	NH.C ₆ H ₅
c.	H	CH ₃
d.	H	(CH ₂) ₃ .CH ₃
e.	OCH ₃	NH.C ₆ H ₅
f.	OCH ₃	CH ₃
g.	OCH ₃	(CH ₂) ₃ .CH ₃

On the other hand, treatment of (VIa and b) with phenylhydrazine in boiling acetic acid was found to give (XVIIIa and b) via condensation and subsequent cyclization.¹²



a.	R	=	H
b.	R	=	OCH ₃

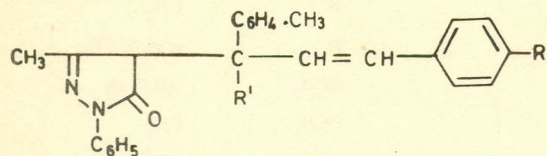
Heating (XVII b and e) with glacial acetic acid gave products which are shown to be identical with (XVIIIa and b) by means of mixed melting point determination and infrared spectrum. In the reaction of (VIa and b) with methylmagnesium iodide, ethylmagnesium iodide, phenylmagnesium bromide and benzylmagnesium chloride one mole of the Grignard reagent is incorporated and the products are (XIX-a-f)^{12,13}



	R	R'
a.	OCH ₃	C ₂ H ₅
b.	OCH ₃	CH ₂ .C ₆ H ₅
c.	OCH ₃	C ₆ H ₅
d.	H	CH ₃
e.	H	C ₂ H ₅
f.	H	C ₆ H ₅

Reaction of (VIIa and b) with Grignard reagents namely methyl magnesium iodide, ethyl magnesium

iodide, phenyl magnesium bromide and *p*-anisyl magnesium bromide (one mole) affected the formation of products (XX a-g) via 1,4 addition to the exocyclic double bond.¹³



XX

	R	R'
a,	H	C ₂ H ₅
b,	H	C ₆ H ₅
c,	H	C ₆ H ₄ OCH ₃
d,	H	CH ₃
e,	OCH ₃	CH ₃
f,	OCH ₃	C ₂ H ₅
g,	OCH ₃	C ₆ H ₅

Experimental

The melting points reported are uncorrected. The I/R spectra (KBr) of the compound were recorded on Unicam sp. 1200 spectrophotometer.

Condensation of 1-Phenyl-3-Methyl-2-Pyrazolin-5-One (I) with Diketones: Formation of IIa - c
A mixture of 1-phenyl-3-methyl-2-pyrazolin-5-one (0.01 mole) and diketone (0.015 mole) was heated in an oil bath at 140° for three hour. The reaction mixture was left to cool and the product formed was triturated with ethanol. The solid that separated was crystallized from the proper solvent, (yield 75%). The results are given in Table 2.

TABLE 1. IR SPECTRA.

Compound	ν cm ⁻¹		
II	1610,	1660	1690
III	1600,	1700	
IV	1616	1660	
VI	1610,	1660	1690
VII	1620,	1630,	1660
VIII	1730,	1680,	1630
IX	1720,	1600	
Xc	1700,	1600	
XI	1730,	3450	
XII	1700,	3000	
XIII	1620,	2950	
XIV	1610,	2950	
XV	1640,	1600	
XVI	1620,	1710	3300
XVII	1620,	1720,	3500
XVIII	1600		
XIX	1715,	1610,	3350
XX	1610,	1730	
XXI	1630,	1720.	

TABLE 2.

Compound	M.p.	Solvent yield%	Formula (mol wt)	Analyses %			
				Found		Calculated	
				C	H	C	H
II a	175	B/P (75)	C ₂₉ H ₂₀ N ₂ O ₂ (428.466)	80.9	4.8	81.3	4.6
II b	140	B 60	C ₂₀ H ₁₈ N ₂ O ₂ (318.360)	75.13	5.3	75.4	5.6
II c	145	B/P 70	C ₁₄ H ₁₄ N ₂ O ₂ (242.268)	69.6	5.9	69.42	5.78
III	174	B 80	C ₁₅ H ₁₃ N ₂ O (237.270)	75.4	5.7	75.90	5.40

B = benzene, B/P (benzene/lightpetrol, 60 - 80).

Condensation of (I) with Benzil : Formation of (IV) The above procedure was followed but using (0.025 mole) 1-phenyl -3-methyl -2-pyrazolin -5-one. The solid obtained after cooling was crystallized from benzene, light petrol (60-80) giving (IV); m.p. 165° (yield 70%). Analysis: Required for $C_{34}H_{26}N_4O_2$: C, 78.16;H,4.9: (522.580) : C, 77.9;H:5.1

Reaction of Chalcones with 1-Phenyl-3-Methyl-2-Pyrazolin-5-One : Formation of (VI) A mixture of (I) (0.1 mole) in ethanol (50 ml) and chalcone (0.1 mole) was heated under reflux with sodium methoxide (0.1 mole). The solid product obtained was crystallized from benzene light petrol (b.p. 40 - 60°) mixture (yield 65%). The results are given in Table 3.

Condensation of 1-Phenyl-3-Methyl-2-Pyrazolin-5-One (I) with Chalcones: Formation of VII a and b) A mixture of 1-phenyl -3-methyl -2-pyrazolin -5-one (0.01 mole) and chalcones (0.01 mole) was heated in an oil bath at 160 °C for three hours. The reaction mixture was left to cool, and the product formed was crystallized from benzene light petrol (b.p 40-60°) mixture. The results are listed in Table 4.

Reaction of (II a and b), (IV) and (VII a and b) with Aromatic Hydrocarbons Formation of (VIII a - g), (IX a - h) and (XXI a - g) To a mixture of 100 ml

of the aromatic hydrocarbon and 10 g of anhydrous aluminium chloride a solution of (II a and b), (IV) or (VII a and b) aromatic hydrocarbon (0.02 mole) was added gradually with stirring. The mixture was heated on a steam bath for 4 hour.

After 15 hour stirring the reaction mixture was allowed to stand over night and then decomposed by dilute hydrochloric acid and the solvent was removed by steam distillation. The solid product obtained was recrystallized from the appropriate solvent to give (VIII a - g), (IXa - h) and (XXI a - g) respectively.

The detailed results are listed in Table 5.

Reaction of (II a and b), (IV), (VI a and b) and (VII a and b) with Grignard Reagents. To 1 g Mg metal in anhydrous ether (30 ml) was added dropwise aryl/ or alkyl halides (0.04 mole) in dry ether (15 ml). The mixture was heated under reflux and compound (11), (IV), (VI) and / or (VII) (0.01 mole) in dry ether (50 ml) was added portionwise during 2 hour. The mixture was refluxed for additional 2 hour left overnight and decomposed with dilute hydrochloric acid, the ethereal layer washed with water and dried with anhydrous $MgSO_4$ and evaporated by air blowing to give a solid which was crytallized from the suitable solvent. The results obtained are given in Table 6.

TABLE 3. MICHAEL ADDUCTS (VL).

Compound	M.p.	Solvent yield %	Formula (mol wt)	Analyses %			
				Found C	H	Calculated C	H
VI a	110	B/P (60)	$C_{26}H_{24}N_2O_2$ (396.468)	78.4	6.0	78.78	6.06
VI b	108	P (65)	$C_{27}H_{25}N_2O_3$ (425.486)	75.7	6.1	76.23	5.88

B/P = Benzene/light petrol (60 - 80), P = light petrol (100-120).

TABLE 4. CONDENSATION OF (I) WITH CHALCONES

Compound	M.p.	Solvent yield %	Formula (mol.wt.)	Analyses %			
				Found C	H	Calculated C	H
VII a	85	P (70)	$C_{26}H_{22}N_2O$ (378.452)	81.95	5.6	82.53	5.8
VII b	120	B/P (50)	$C_{27}H_{24}N_2O_2$ (408.478)	78.9	5.65	79.41	5.88

B/P = Benzene/light petrol (40 - 60), P = light petrol (60 - 80).

TABLE 5. FRIEDEL CRAFT ADDUCTS (VII),(IX) and (XX).

Compound	M.p.	Solvent yield %	Formula (mol.wt.)	Analyses %			
				Found		Calculated	
				C	H	C	H
VIII a	78	E (40)	$C_{31}H_{26}N_2O_3$ (474.534)	78.2	5.7	78.48	5.48
b	95	B/P (50)	$C_{33}H_{30}N_2O_2$ (486.586)	81.13	6.3	81.48	6.17
c	117	B/P (45)	$C_{30}H_{23}N_2O_2Cl$ (479.000)	75.0	4.7	75.23	4.8
d	over 300	E (40)	$C_{31}H_{25}N_2O_2Cl$ (493.026)	75.23	5.2	75.53	5.07
e	160	B/P (55)	$C_{30}H_{24}N_2O_2$ (444.508)	80.6	5.5	81.08	5.4
f	150	B/P (60)	$C_{26}H_{24}N_2O_2$ (396.468)	78.4	5.7	78.78	6.06
g	160	P (50)	$C_{26}H_{23}N_2O_2Cl$ (430.960)	72.6	5.4	72.47	5.34
IX a	230	E (50)	$C_{46}H_{37}N_4O_2$ (677.788)	81.0	5.5	81.53	5.46
b	150	P (60)	$C_{50}H_{46}N_4O_2$ (734.900)	81.25	6.4	81.74	6.26
c	300	E (50)	$C_{46}H_{36}N_4O_2Cl_2$ (747.780)	73.5	4.9	73.89	4.81
d	145	E (55)	$C_{48}H_{42}N_4O_2$ (706.848)	81.2	5.9	81.58	5.94
e	220	E (60)	$C_{48}H_{40}N_4O_2Cl_2$ (774.832)	74.6	5.3	74.41	5.16
f	130	B/P (50)	$C_{52}H_{50}N_4O_2$ (762.952)	82.1	6.6	81.88	6.56
g	180	E (60)	$C_{48}H_{46}N_4O_2$ (710.880)	81.0	6.5	81.12	6.47
h	85	E (40)	$C_{48}H_{42}N_4O_4$ (738.848)	77.85	6.0	78.04	5.69
XXI a	145	B/P (55)	$C_{33}H_{30}N_2O$ (470.586)	83.9	6.4	84.25	6.38
b	110	P (60)	$C_{34}H_{32}N_2O$ (484.612)	84.5	6.7	84.29	6.61

continued

Table 5, continued

c	130	P (50)	$C_{32}H_{27}N_2OCl$ (490.552)	77.92	5.5	78.28	5.70
d	140	B/P (60)	$C_{34}H_{32}N_2O_3$ (516.612)	79.2	6.4	79.06	6.20
e	115	B (50)	$C_{34}H_{32}N_2O_2$ (500.612)	81.8	6.6	81.6	6.4
f	132	P (40)	$C_{33}H_{29}N_2O_2Cl$ (520.578)	75.7	5.7	76.08	5.57
g	120	B/P (50)	$C_{35}H_{34}N_2O_2$ (514.638)	81.44	6.8	81.71	6.61

B = benzene, B/P = benzene/light petrol (60-80),
P = light petrol (80-100). E = ethanol.

TABLE 6, ADDUCTS OF GRIGNARD REACTION (X a - d), (XI), (XII), AND (XIX)

Compound	M.p.	Solvent yield %	Formula (mol.wt.)	Analyses		% Calculated	
				Found C	H	C	H
X a	220	E (60)	$C_{36}H_{34}N_4O_2$ (554.664)	78.1	6.7	77.97	6.13
b	120	B/P (65)	$C_{38}H_{38}N_4O_2$ (582.716)	77.5	6.7	78.35	6.51
c	175	E (60)	$C_{48}H_{42}N_4O_2$ (706.848)	80.9	5.9	81.58	5.94
d	115	B/P (50)	$C_{46}H_{50}N_4O_2$ (690.892)	79.60	6.8	80.00	7.24
XI a	195	E (40)	$C_{26}H_{26}N_2O_2$ (398.484)	78.1	6.2	78.39	6.53
b	145	E (50)	$C_{28}H_{30}N_2O_2$ (426.536)	79.3	6.8	78.8	7.04
c	182	A (45)	$C_{38}H_{34}N_2O_2$ (550.668)	82.6	5.8	82.9	6.18
d	260	E (40)	$C_{38}H_{34}N_2O_2$ (550.668)	82.8	5.9	82.9	6.18
e	250	B (55)	$C_{36}H_{30}N_2O_2$ (522.616)	82.3	5.5	82.75	5.74
XII a	130	P (40)	$C_{22}H_{26}N_2O_2$ (350.444)	75.2	7.2	75.42	7.42

continued

Table 6. continued

	b	110	B (50)	$C_{34}H_{34}N_2O_2$ (502.628)	81.0	6.6	81.27	6.77
XVIII	a	90	P (40)	$C_{32}H_{28}N_4$ (468.576)	82.2	6.1	82.05	5.98
	b	100	P/P (60)	$C_{33}H_{32}N_4O_2$ (516.618)	76.54	6.0	76.74	6.2
XIX	a	98	P (50)	$C_{29}H_{32}N_2O_3$ (456.562)	76.0	6.8	76.31	7.01
	b	150	B/P (40)	$C_{34}H_{34}N_2O_3$ (518.668)	78.4	6.4	78.76	6.56
	c	92	P (50)	$C_{33}H_{32}N_2O_3$ (504.602)	78.7	6.2	78.57	6.34
	d	80	P (40)	$C_{27}H_{28}N_2O_2$ (412.510)	78.8	6.6	78.64	6.79
	e	120	B/P (50)	$C_{28}H_{30}N_2O_2$ (426.536)	78.6	7.1	78.87	7.04
	f	100	P (40)	$C_{32}H_{30}N_2O_2$ (474.576)	81.3	6.5	81.01	6.32
XX	a	105	B/P (60)	$C_{28}H_{28}N_2O$ (408.520)	82.5	7.1	82.35	6.86
	b	150	B/P (50)	$C_{32}H_{28}N_2O$ (456.560)	84.3	6.4	84.21	6.14
	c	108	P (60)	$C_{32}H_{30}N_2O_2$ (474.576)	80.8	6.5	81.01	6.32
	d	118	B/P (40)	$C_{27}H_{26}N_2O$ (394.494)	82.5	6.7	82.23	6.59
	e	145	B/P (50)	$C_{28}H_{28}N_2O_2$ (424.520)	79.5	6.3	79.24	6.6
	f	130	P (45)	$C_{29}H_{30}N_2O_2$ (438.546)	79.16	6.62	79.45	6.84
	g	125	B/P (50)	$C_{33}H_{30}N_2O_2$ (486.586)	81.2	6.3	81.48	6.17

Reaction of III with Hydroxyl Amine Hydrochloride. Formation of (XIV). To an alcoholic solution of hydroxyl amine hydrochloride (2g/20 ml) was added a solution of 2.5 g sodium acetate in the least amount of hot acetic acid. This mixture was added to a solution

of III (0.01 mole) in ethyl alcohol (20 ml). The reaction mixture was refluxed for 8 hours, then diluted with water. The solid that separated was crystallized from ethanol to give (XIV) as colourless crystals, m.p. 300° , yield 70%.

TABLE 7.

Compound	M.p.	Solvent yield %	Formula (mol.wt.)	Analyses %			
				Found		Calculated	
				C	H	C	H
XIII a	over300	E	C ₁₅ H ₁₆ N ₄	71.2	6.5	71.4	6.3
		(50)	(252.310)				
b	197	B	C ₂₁ H ₂₀ N ₄	77.1	6.0	76.8	6.0
		(65)	(328.402)				
XVI	90	B	C ₁₄ H ₁₆ N ₄ O	65.7	6.3	65.62	6.25
		(75)	(256.300)				
XVII a	135	B/P	C ₂₆ H ₂₆ N ₄ O	75.9	6.5	76.0	6.3
		(60)	(410.500)				
b	100	P	C ₃₂ H ₃₀ N ₄ O	78.8	6.2	79.0	6.1
		(50)	(486.592)				
c	120	B	C ₂₇ H ₂₇ N ₃ O	79.4	6.7	79.2	6.6
		(40)	(409.510)				
d	90	B/P	C ₂₄ H ₂₈ N ₃ O	79.30	7.1	79.6	7.3
		(60)	(374.488)				
e	130	B/P	C ₃₃ N ₃₂ N ₄ O ₂	76.45	6.1	76.74	6.2
		(50)	(516.618)				
f	120	P	C ₂₈ H ₂₈ N ₃ O ₂	76.36	6.1	76.7	6.3
		(40)	(438.528)				
g	90	B/P	C ₃₁ H ₃₅ N ₃ O ₂	77.4	7.0	77.33	7.27
		(60)	(481.614)				
XV a	152	B/P	C ₁₆ H ₁₈ N ₃	76.3	7.2	76.1	7.1
		(40)	(252.328)				
XV b	160	B	C ₂₂ H ₂₁ N ₃	80.4	6.5	80.7	6.4
		(75)					

B = benzene; B/P = benzene/light petrol (60 - 80); P = light petrol (80 - 100); E = ethanol.

Analysis: Found : C, 70.9;H, 6.1 C₁₅H₁₅N₃O;
requires: C, 71.1;H,5.9 (253.294)

Action of Hydrazines, and / or Amines on (II e), (III) and (VI a and b). A solution of (II c), (III) or (VI a and b) (0.01 mole) in ethyl alcohol 20 ml was treated with hydrazine hydrate, phenylhydrazine and/or amines (0.03 mole) and the reaction mixture was refluxed for 6 hour. The products that separated on cooling were crystallized from a suitable solvent.

The results obtained are given in Table 7.

Action of Phenyl Hydrazine on (VI a and b) in Boiling Glacial Acetic Acid : Formation of (XVIII) a and b). A solution of equimolecular amounts of phenyl hydrazine and (VI a and b) in glacial acetic acid was heated under reflux for 5 hours. The product that separated on cooling was crystallized from the suitable solvent to give (XVIII a and b). The results obtained are given in Table 6.

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