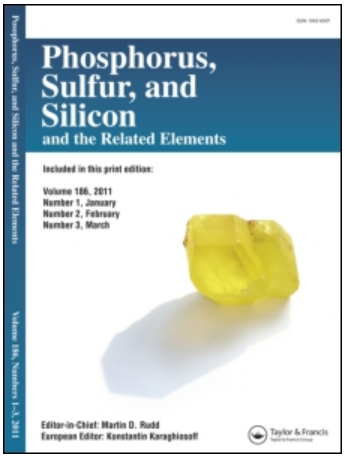

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STUDIES ON CHROMONES AND XANTHONE DERIVATIVES

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STUDIES ON CHROMONES AND XANTHONE DERIVATIVES

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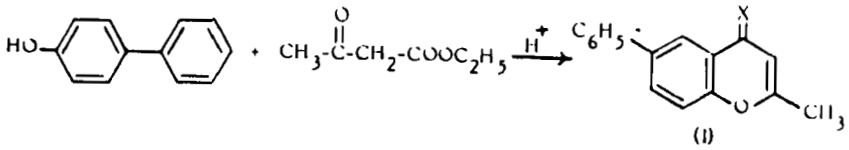
2-Methyl-6-phenyl chromone **Ia** and a variety of its derivatives were synthesized. The reactivity of **Ia** and other chromones with aromatic aldehydes, hydrazine hydrate, hydrazine derivatives, hydroxylamine hydrochloride, different primary amines and Grignard reagents was investigated. The I.R. and H^1NMR spectra of the products are discussed.

Key words: Nitrogen nucleophiles; Grignard reagents with chromone; thiochromone and xanthone derivatives.

Chromones and their derivatives have been receiving great attention. Some derivatives of chromones proved to have pronounced effects on nervous activity[1] and were used as spasmolytic and as coronary dilators.[2] Some members were reported to reduced blood pressure as antihypertensive agents[3] and act as diuretics,[4] antiallergic[5,6] and antibiotics.[7] In the course of the present work, several derivatives containing the chromone moiety were prepared and some of their reactions were investigated. The aim was to show the reactivity of chromone nucleus towards cycloaddition reactions and the behaviour of the chromone moiety towards nucleophilic reagents.

When 4-hydroxybiphenyl was treated with ethyl acetoacetate in the presence of concentrated sulphuric acid, 2-methyl-6-phenyl chromone **Ia** was obtained in a good yield as the major product. The I.R. spectrum of **Ia** displays no OH band and showed bands at 1650 cm^{-1} (νC=O of γ-pyrone). The H^1NMR spectrum of **Ia** ($CDCl_3$) showed signals at δ 7.8 (m, 8H, aromatic protons), δ 6.4 (s, 1H, olefinic proton) and δ 3.2 (s, 3H, CH_3-). The methyl group in the 2-position condenses easily with aromatic aldehydes, namely, benzaldehyde, *N,N*-dimethyl *p*-aminobenzaldehyde and cinnamaldehyde to give the 2-styryl derivatives **IIa–c**.

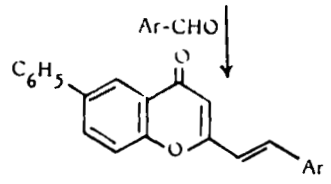
The 2-styryl derivatives **IIa–c** react as dienes undergoing Diel's–Alder reactions with maleic anhydride to give the xanthone derivatives **IIIa–c**. The structure of **III** was based on the similarity to other xanthone derivatives prepared by this method[8,9,10] and on the I.R measurements. Compound III showed two bands at 1808 and 1770 cm^{-1} resulting from asymmetrical modes of >C=O, 1685 cm^{-1} for νC=O of γ-pyrone. However, the structures of **IIIa, b** were supported by the H^1NMR spectra ($CDCl_3$) which were consistent with their proposed structure. **IIIa** showed the following signals at δ 7.8–7.1 (m, 14H, Ar—H + olefinic proton), and δ 0.9–3.2 (m, 4H, cyclohexene ring protons). **IIIb** showed signals at δ 7.6–7.0 (m, 13H, Ar-H + olefinic proton), δ 2.9 (s, 6H, —$N(CH_3)_2$] and δ 0.9–



(I)

a, X = O

b, = S



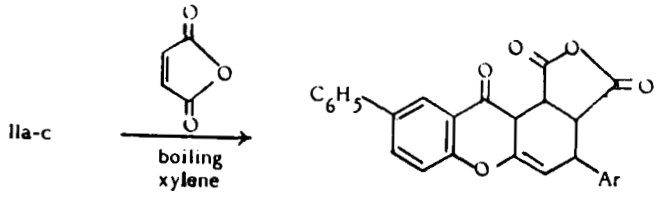
(II)

a, Ar = C_6H_5-

b, = $(CH_3)_2N$-C_6H_4-p

c, = -CH=CH-C_6H_5

2.6 (m, 4H, cyclohexene ring protons). The structure of **IIIc** was confirmed besides the correct analytical data (Table II) and I.R spectrum via the following chemical reactions: i) hydrolysis of **IIIc** with ethanolic potassium hydroxide gave the corresponding dicarboxylic acid **IVa**. ii) Treatment of **IIIc** with absolute ethanol in the presence of HCl gas gave the corresponding ester **IVb**.



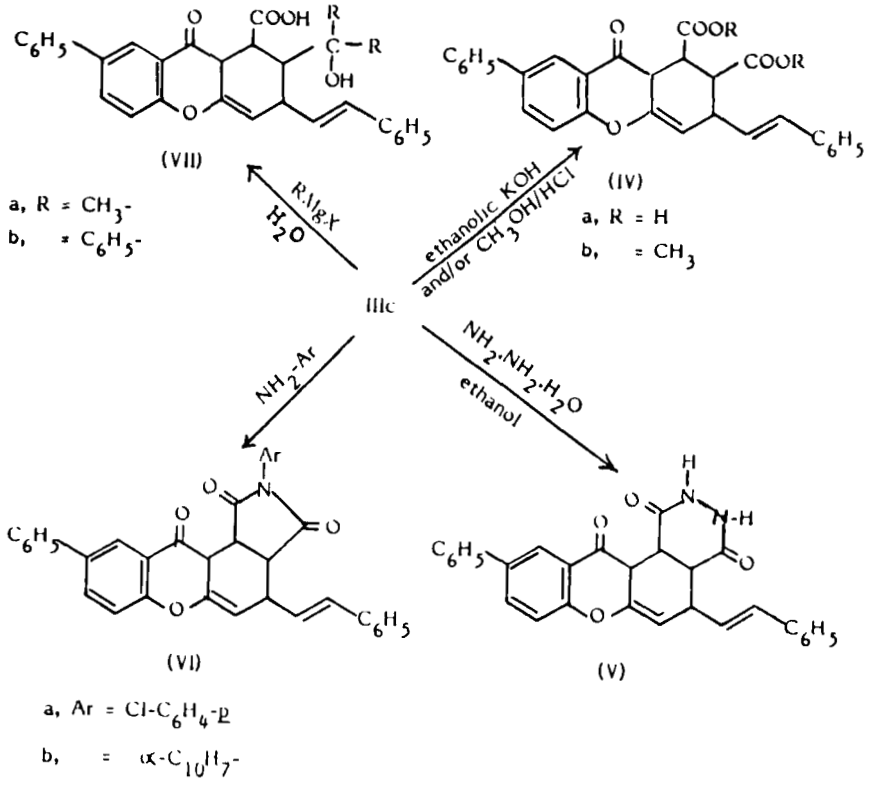
(III)

a, Ar = C_6H_5-

b, = $(CH_3)_2N$-C_6H_4-p

c, = -CH=CH-C_6H_5

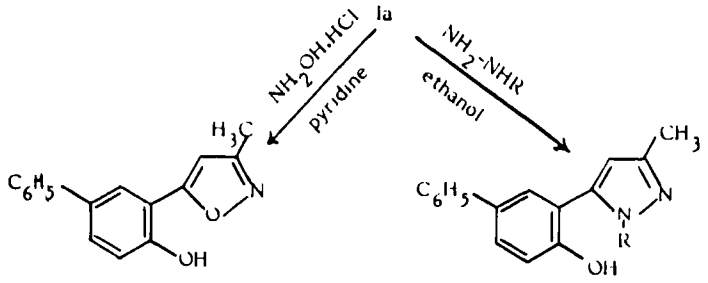
The xanthone derivative **IIIc** was reacted with hydrazine hydrate in boiling ethanol and afforded the 1,4-phthalazindione derivative V which exists in a lactam-lactim dynamic equilibrium. The structure of V was established from the following evidence: a) correct elemental analysis, b) the I.R spectrum exhibits well defined absorption bands at 1692, 1645, 1620, 1605, 3280, 3310 and 3410 cm^{-1} attributed to νC=O (1,4-phthalazindione), νC=O (γ-pyrone), νC=N, νC=C, νNH and νOH, respectively.



The action of primary aromatic amines, such as, *p*-chloroaniline and α-naphthylamine on **IIIc** gave the *N*-aryl derivative **VIa, b**. The I.R spectrum of **VI** showed νC=O (imide) at 1720-1680 cm^{-1} and νC=O (γ-pyrone) at 1660 cm^{-1}. Furthermore, treatment of **IIIc** with methyl-magnesium iodide and phenylmagnesium bromide afforded the carbinol derivative **VIIa, b**. The I.R spectra of compounds **VIIa** and **b** were examined and were found to be consistent with the proposed structures. Compound **VIIa** displayed νC=O 1710 cm^{-1} (acid), νC=O at 1680 cm^{-1} (γ-pyrone), νOH (br) 3500–3270 cm^{-1}. The H^1NMR spectrum of **VIIa** ($CDCl_3$) showed signals at δ 7.6 (m, 14H, Ar—H + olefinic ring proton), δ 6.1 (s, 2H, olefinic protons), δ 4.1 (br.s, 1H, 3° alcohol), δ 0.9–3.2 (m, 4H, cyclohexene ring protons).

Reaction of 2-methyl 6-phenyl chromone **Ia** with excessive hydroxylamine hydrochloride in the presence of pyridine took place through cleavage of the pyrone ring and gave the corresponding isoxazole derivative **VIII**. The structure of **VIII** was established from the following arguments: i) Correct analytical data (Table V). ii) The isoxazole **VIII** gave a violet colour with ferric chloride indicating the free phenolic hydroxyl group. iii) The I.R spectrum shows characteristic absorption bands 1610, 1605 and 3450 cm^{-1} due to νC=N, νC=C and νOH, respectively. iv) The H^1NMR of **VIII** showed the following signals: δ at 7.9–7.2 (m, 8H, aromatic protons), δ 6.2 (br.s, 1H, olefinic proton of isoxazole ring), δ 4.3 (s, 1H, hydroxyl group) and δ 2.3 (s, 3H, CH_3). Similarly, **Ia** reacted with hydrazine hydrate and/or phenylhydrazine in boiling ethanol to give the

pyrazole derivative **IXa, b**. Compound **IX** gave the characteristic colour reaction of pyrazoles with ferric chloride solution. The I.R spectrum of **IX** exhibited strong absorption bands at *ca* 1620, 1600 and 3210, 3430 cm^{-1} which were attributable to $\nu C{=}N$, $\nu C{=}C$ and νNH, OH, respectively, with disappearance of $\nu C{=}O$ (chromone).

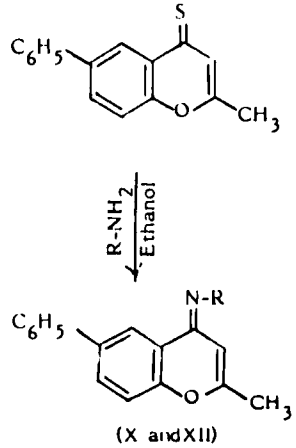


(VIII) (IX)

a, R = H

b, = C_6H_5-

2-Methyl-6-phenyl chromone-4-thione **Ib** was prepared by heating **Ia** with phosphorous pentasulphide in dry benzene. **Ib** showed characteristic colour reaction with mercuric chloride.[11] The I.R spectrum displayed $\nu C{=}S$ at 1350 cm^{-1} and the absence of $\nu C{=}O$ chromone. The thione **Ib** was subjected to react with hydrazine hydrate, phenylhydrazine and/or *p*-nitrophenylhydrazine at room temperature and gave the hydrazone derivative **Xa–c**. The structure of the hydrazone **Xa** was based on the following assignments: a) hydrolysis of **Xa** with 5% HCl afforded **Ia**; b) reacts with **Ib** to give azine **XI**; c) it does not give a colour reaction with ferric chloride; d) gives the colour reaction of hydrazones. e)

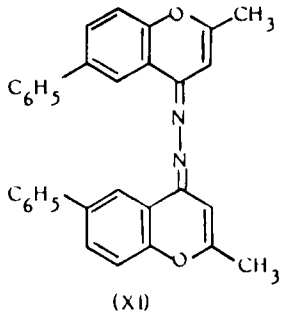


(X and XII)

X a; R = NH_2 ; b, R = NH-C_6H_5 ; c, R = NH-C_6H_4-NO_2-4

XII a; R = 2-Pyridyl ; b, R = C_6H_5-N=N-C_6H_4-4

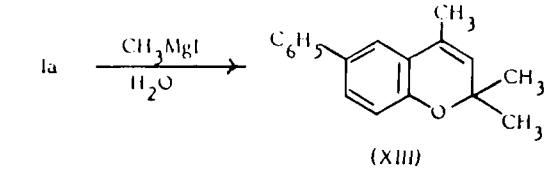
The I.R. spectrum of **Xa** showed the following characteristic vibrations νC=N at 1624 cm^{-1} and 1605 cm^{-1} (νC=C). f) The H^1NMR spectrum of **Xa** ($CDCl_3$) showed the following signals: δ at 8.1 (br.s, 2H, =N—NH_2), δ 7.8–7.1 (m, 8H, aromatic protons), δ 6.1 (s, 1H, olefinic proton) and δ 2.6 (s, 3H, CH_3-).



(XI)

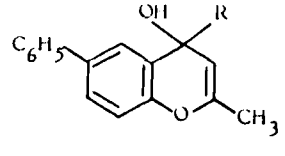
On the other hand, treatment of **Ib** with primary aromatic amines such as 2-aminopyridine and *p*-aminoazobenzene afforded the imino derivatives **XIIa, b**. The I.R spectrum of **XII** showed the disappearance of νC=S and only νC=N at 1620–1610 cm^{-1}.

Both aliphatic and aromatic Grignard reagents add to chromones[12,13,14] to give γ-chromenols which are easily converted by acid to benzopyrillium salts. Methylmagnesium iodide reacts with **Ia** and gave benzopyrane derivative **XIII**.



(XIII)

The N^1NMR of **XIII** showed the following signals: δ at 7.6–7.0 (m, 8H, aromatic protons), δ 6.4 (br.s, 1H, olefinic proton), δ 3.2 (s, 3H, CH_3) and δ 2.1 $\left(s, 6H, >C<^{CH_3}_{CH_3}\right)$. Furthermore, the reaction of thione **Ib** with phenyl- and/or cyclohexyl magnesium bromide afforded the benzopyran-4-ol derivatives **XIVa, b**. The I.R spectrum of **XIV** displayed νOH at 3540–3460 cm^{-1} and ωC=C at 1605 cm^{-1}. The H^1NMR of **XIVb** showed the following signals: δ at 7.8–7.2 (m, 8H, aromatic protons), δ 6.3 (s, 1H, olefinic proton), δ 3.1 (s, 1H, hydroxyl group), δ 2.8 (s, 3H, CH_3) and δ 1.2–1.7 (m, 11H, cyclohexane ring).



(XIV)

a, R = C_6H_5-

b, R = C_6H_{11}-

EXPERIMENTAL

The I.R spectra were determined with a Perkin-Elmer Infrared spectrophotometer using KBr Wafer technique. The H^1NMR spectra were determined on 5% solutions of $CDCl_3$ at 60 MC with a Varian associates Model V 4300 B spectrophotometer using tetramethyl silane as internal reference. All m.p. are uncorrected.

2-Methyl-6-phenyl chromone **Ia** A mixture of 4-hydroxy biphenyl (0.01 mole), ethyl acetoacetate (0.01 mole) and concentrated sulphuric acid (10 ml) was kept in a freezing mixture (ice-NaCl) for one hr., the temperature was kept below 10°C. The dark red solution was cautiously poured into ice/water. The solid obtained was filtered off, then crystallized from light petrol (110–120°) to give the starting chromone **Ia** as a yellow crystals, m.p. 145–7°. $C_{16}H_{12}O_2$(236), calcd. C, 81.4; H, 5.08; Found, C, 81.6; H, 5.0.

Action of P_2S_5 on **Ia** *Formation of* **Ib** Compound **Ib** was obtained by refluxing a solution of 2-methyl-6-phenyl chromone **Ia** (1 g) in dry benzene (50 ml) with phosphorous pentasulphide (1 g) for 2 hr. The reaction mixture was filtered while hot, the solvent was evaporated and the product recrystallized from toluene as red needles, m.p. 196°C, yield 52%. $C_{16}H_{12}OS$ (252), Calcd. C, 76.2; H, 4.8, S, 12.3; Found C, 76.3; H, 5.0; S, 12.8.

Condensation of **Ia** *with aromatic aldehydes: Formation of* **IIa–c** The chromone **Ia** (0.001 mole) was dissolved in a minimum amount of absolute ethanol and treated at room temperature with an alcoholic solution of sodium ethoxide (0.001 mole). The appropriate aldehyde (0.001 mole) was then added and the mixture was kept for 24 hr at room temperature. The yellow condensation product was filtered off and recrystallized from the proper solvent to give the 2-styryl derivatives **IIa–c**.

Reaction of 2-styryl chromones **IIa, b** *and* **c** *with maleic anhydride* A mixture of each of **IIa, b** and **c** (0.002 mole), maleic anhydride (0.02 mole) and dry xylene (25 ml) was refluxed for 32 hr. The solids formed after cooling were filtered and recrystallized from toluene to give the adducts **IIIa, b** and **c** listed in Table II.

TABLE I

Condensation of **Ia** with aromatic aldehydes

Compd.	M.P°C	Solvent of cryst *n*	Yield %	Formula (mol. wt)	Analysis % calcd/found C	H	N
IIa	216	Ethanol	62	$C_{23}H_{16}O_2$	85.2	4.9	—
				(324)	85.3	5.0	—
IIb	203	Benzene	76	$C_{25}H_{21}NO_2$	81.7	5.7	3.8
				(367)	81.6	5.9	4.0
IIc	242	Ethanol	80	$C_{25}H_{18}O_2$	85.7	5.1	—
				(350)	85.3	5.1	—

TABLE II

Reaction of 2-styryl chromones **IIa, b** and **c** with maleic anhydride

Compd.	M.p.°C	Yield %	Formula (mol. wt)	Analysis % calcd/found C	H	N
IIIa	294	48	$C_{27}H_{18}O_5$	76.8	4.3	—
			(422)	76.6	4.4	—
IIIb	310	36	$C_{29}H_{23}NO_5$	74.8	4.9	3.0
			(465)	74.7	5.0	2.8
IIIc	286	52	$C_{29}H_{20}O_5$	77.7	4.5	
			(448)	77.9	4.2	—

TABLE III

Action of hydrazine hydrate and/or primary aromatic amines on **IIc**

Compd.	M.p.°C	Solvent of cryst *n*	Yield %	Formula (mol. wt)	Analysis % calcd/found C	H	N	Cl
V	320	*n*-Butanol	54	$C_{29}H_{22}N_2O_4$ (462)	75.3 75.1	4.8 4.7	6.1 6.3	— —
VIa	235	Toluene	46	$C_{35}H_{24}ClNO_4$ (557.5)	75.3 75.6	4.3 4.1	2.5 2.7	6.4 6.6
VIb	219	Benzene	38	$C_{39}H_{27}NO_4$ (573)	81.7 81.5	4.7 4.8	2.4 2.6	— —

Hydrolysis of **IIIc:** Formation of **IVa** The Diels–Alder adduct **IIIc** (0.5 g) was refluxed with 10% aqueous alcoholic potassium hydroxide (10 m) for 3 hr. The cold mixture was acidified with diluted HCl and the solid deposited was filtered off, dried and then crystallized from ethanol to give the diacid **IVa**, m.p; 330, Yield 92%. $C_{29}H_{22}O_6$ (466), Calcd. C, 74.7; H, 4.7; Found, C, 74.6; H, 4.9.

Ethanolysis of xanthone derivative **IIIc:** *Formation of* **IVb** Xanthone derivative **IIIc** (0.003 mole) was suspended in 50 ml of absolute ethanol and hydrogen chloride gas is passed into the suspension for 1 hr. The cold yellow solution was diluted with water. The solid separated was filtered off, dried and then crystallized from benzene yielding the desired diester **IVb**, m.p. 203, $C_{31}H_{26}O_6$ (494), Calcd. C, 75.3; H. 5.3; Found, C, 75.3; H, 5.1.

Action of hydraxine hydrate and/or primary aromatic amines on **IIIc:** *Formation of* **V** *and* **VIa, b** A mixture of **IIIc** (0.003 mole, 1.1 g) and hydrazine hydrate (0.006 mole, 0.4 ml) and/or the appropriate primary aromatic amine, namely *p*-chloroaniline and α-naphthylamine was heated under reflux in glacial acetic cid (20 ml) for 6 hr. After cooling, the reaction mixture was diluted with water and the solid separated was filtered off and crystallized from a suitable solvent to give **V** and **VIa, b,** respectively. Listed in Table III.

Reaction of **Ia, Ib** *and* **IIIc** *with Grignard reagents: Formation of* **XIII, XIVa, b** *and* **VIIa, b** An ethereal solution of aryl- (or alkyl) magnesium halide (0.03 mole) was added dropwise to a solution of **Ia** or **b** or **IIIc** (0.01 mole) in dry benzene, in the course of 30 min. The reaction mixture was refluxed for 6 hrs during which the ether was allowed to evaporate, left overnight, decomposed with ice-cold saturated ammonium chloride solution and extracted with ether. The ethereal layer was washed with water, dried (anhydrous sodium sulphate), and evaporated by air blowing, to give an oil which was triturated with light petrol (60–80°). The crude solid obtained was crystallized from the appropriate solvent to give **XIII, XIVa, b** and **VIIa, b**, respectively. The products are listed in Table IV.

TABLE IV

Action of Grignard reagents on **IIIc, Ia** and **b**

Compd.	M.p.°C	Solvent	Yield %	Formula (mol. wt)	Analysis % calcd/found C	H
VIIa	136	Bz/P	36	$C_{31}H_{28}O_5$ (480)	77.5 77.7	5.8 5.8
VIIb	182	Bz/P	34	$C_{41}H_{32}O_5$ (604)	81.5 81.4	5.3 5.5
XIII	170	P	58	$C_{18}H_{18}O$ (250)	86.4 86.6	7.2 7.3
XIVa	253	Bz/M	62	$C_{22}H_{18}O_2$ (314)	84.1 84.2	5.7 5.6
XIVb	175	Bz/P	66	$C_{22}H_{24}O_2$ (320)	82.5 82.6	7.5 7.5

* Bz = benzene; P = light petrol (100–120°) and M = methanol

TABLE V

Action of hydroxylamine and hydrazine derivative on **Ia**

Compd.	M.p.°C	Solvent of cryst *n*	Yield %	Formula (mol. wt.)	Analysis % calcd/found C	H	N
VIII	220	Ethanol	68	$C_{16}H_{13}NO_2$	76.5	5.2	5.6
				(251)	76.7	5.1	5.8
IXa	172	Toluene	53	$C_{16}H_{14}N_2O$	76.8	5.6	11.2
				(250)	76.7	5.5	11.4
IXb	186	Benzene	56	$C_{22}H_{18}N_2O$	80.9	5.5	8.6
				(326)	81.1	5.6	8.6

Action of hydroxylamine hydrochloride on **Ia** A mixture of 2-methyl-6-phenyl chromone **Ia** (0.003 mole) in pyridine (20 ml) and hydroxylamine hydrochloride (excess, 1 g) in water (5 ml) was refluxed for 4 hr. The cooled mixture was acidified with dilute acetic acid and the solid deposited was filtered off and crystallized from ethanol to give the isoxazole derivative **VIII** as colourless needles. (see Table V).

Action of hydrazine hydrate and phenylhydrazine on **Ia:** *Formation of* **IXa, b** To a solution of **Ia** (0.003 mole) in ethanol (20 ml) a solution of hydrazine hydrate and/or phenylhydrazine (excess, 2 ml) in warm ethanol (15 ml) was added. The reaction mixture was heated for 15 min, cooled, diluted with water and the solid which separated was crystallized from the proper solvent to give the pyrazole derivatives **IXa, b**. The products are listed in Table V.

Action of hydrazine hydrate, phenylhydrazine, p-nitrophenylhydrazine and primary aromatic amines on **Ib:** *Formation of* **Xa–c** *and* **XIIa, b** A mixture of **Ib** (0.02 mole) in ethanol (30 ml) and hydrazine derivative or the appropriate primary aromatic amines namely, 2-aminopyridine or *p*-aminoazobenzene (0.06 mole) was refluxed for 4 hr and kept overnight at room temperature. The separated product was filtered off and recrystallized from ethanol to give **Xa–c** and **XIIa, b**, respectively. The products listed in Table VI.

Hydrolysis of hydrazone **Xa** **Xa** (1 g) in ethanol (50 ml) was added dropwise to boiling 5% hydrochloric acid (100 ml) during 15 min. On cooling the dilution effected the separation of **Ia**. The crystallized product (0.5 g, 61 %) had m.p. 145° alone or in admixture with an authentic sample of **Ia**.

Formation of azine **XI** **Xa** (1.4 g, 0.005 mole) and **Ib** (1.3 g, 0.005 mole) were refluxed in ethanol (40 ml) in the presence of 96 % acetic acid (2.ml) for one hr. The yellow needles were separated and

TABLE VI

Action of hydrazine derivatives and primary aromatic amines on **Ib**

Compd	M.p.°C	Yield %	Formula	Analysis % calcd/found C	H	N
Xa	262	60	$C_{16}H_{14}N_2O$	76.8	5.6	11.2
			(250)	76.7	5.6	11.3
Xb	215	64	$C_{22}H_{18}N_2O$	80.9	5.5	8.6
			(326)	80.6	5.6	8.7
Xc	310	38	$C_{22}H_{17}N_3O_3$	71.2	4.6	11.3
			(371)	71.4	4.6	11.1
XIIa	232	72	$C_{21}H_{16}N_2O$	80.8	5.1	8.9
			(312)	80.9	5.3	9.1
XIIb	240	76	$C_{28}H_{21}N_3O$	80.9	5.1	10.1
			(415)	81.0	4.9	10.3

recrystallized from ethanol to give the azine **XI**, m.p. 306°C. $C_{32}H_{24}N_2O_2$ (468), Calcd. C, 82.05; H, 5.1; Found C, 81.9; H, 5.2.

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