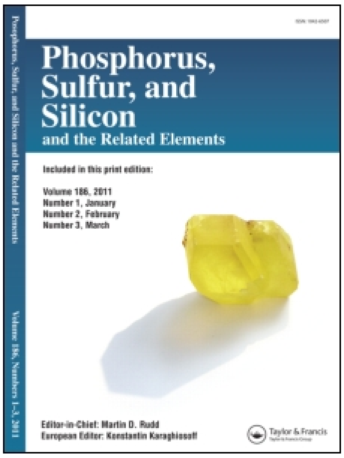

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SOME REACTIONS OF 2-(*p*-CHLOROPHENYL)-4H-1,3-BENZOTHIAZIN-4-THIONE AND 2-(*p*-CHLOROPHENYL)-4H-1,3-BENZOXAZIN-4-ONE

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The reaction of 1,3-benzoxazin-4-one (**1**) and 1,3-benzothiazin-4-thione (**2**) with alkyl, aralkyl and/or aralkyl magnesium halides has been described. Primary amines condensed with (**2**) and (**1**) giving the corresponding Schiff's bases (**3a–d**) or (**4a–d**) respectively. Compounds (**2**) and (**1**) reacted with Grignard reagents with cleavage of C—S bond and C—O bond to yield 4-(ethyl or phenyl)-1,3 benzothiazin-4-thiol (5a and 5b) or 2-(*p*-Chlorophenyl)-4-(ethyl, or phenyl)-4-hydroxy-4H-1,3-benzoxazin (6a and 6b) respectively. On the other hand (**1**) reacted with benzyl Chloride under the Grignard reaction conditions and gave 2-(*p*-Chlorophenyl)-4-benzylidene-1,3 benzoxazine (**7**). Also with hydrazine hydrate (**1**) reacted to give the triazole derivative (**8**). But (**1**) condensed with *p*-nitrophenylhydrazine and hydroxylamine and yielded the corresponding hydrazone and oxime derivatives (**9a–b**). On the other hand, compound (**2**) reacted with ammonia derivatives and gave the condensation products (**10a–d**).

The compound 2-(*p*-chlorophenyl)-4*H*-1,3-benzothiazin-4-thione (2) was obtained by the action of P_2S_5 in dry xylene on 2-(*p*-chlorophenyl)-4*H*-1,3-benzoxazin-4-one (**1**).[1–3]

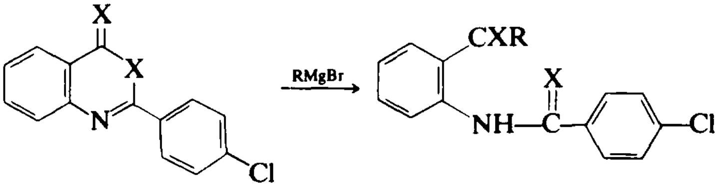
In the present work, I have shown that in contrast to 4*H*-3,1-benzo-thiazine-4-thiones, 4*H*-3,1-benzoxazin-4-ones undergo ring opening by treatment with amines.[5,6] Compound (**2**) reacts with primary amines, namely ethylamine, benzylamine, *p*-toluidine or *o*-chloroaniline in boiling alcohol to yield the corresponding Schiff bases N-2-(*p*-chloro-phenyl)-1,-3-benzothiazin-4-ylidenes (**3a–d**) respectively.

The structures of (**3a–d**) were based on the following evidence:

1) The infrared spectra showed a band at 1635–1640 cm^{-1} due to ν C=N.

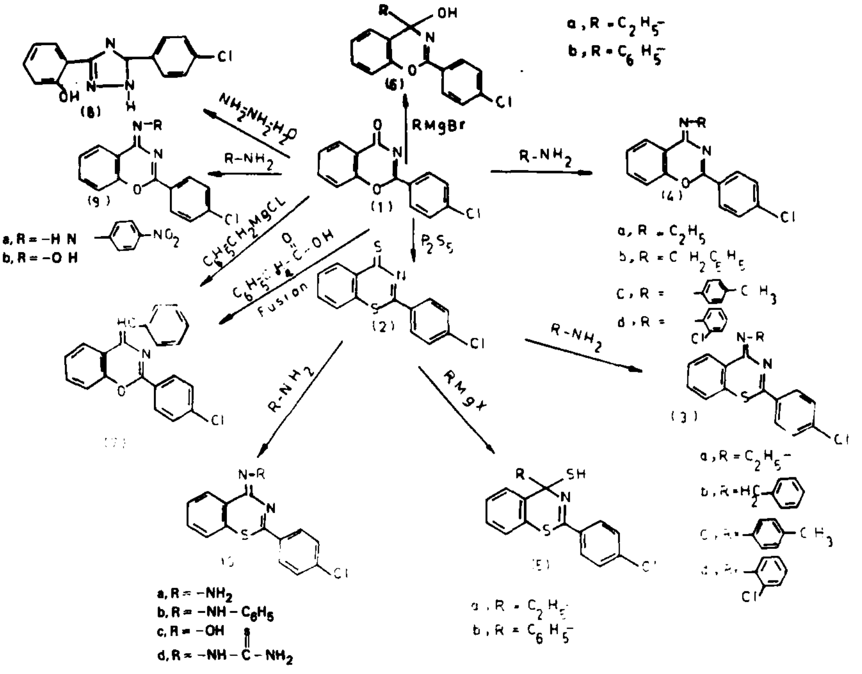
2) ^{1}H-NMR spectrum of **3b** shows signals at δ ppm 3.3 (*s*, 2H; NCH_2Ph), and at 7.2–7.5 (m, 13H aromatic protons).

Similarly 2-(*p*-chlorophenyl)-4*H*-1,3-benzoxazin-4-one (**1**) condensed with the same primary amines under the same conditions and gave N-2-(*p*-chlorophenyl)-1,3-benzoxazin-4-ylidenes (**4a–d**). The infrared spectra of (**4a–d**) exhibited bands attributable to ν C=N at 1630–1645 cm^{-1}. Also, whereas 3,1-benzoxazine-4-one or their thiones underwent ring opening with Grignard reagents[1]



X = S or O   R = C_2H_5 or C_6H_5

In the present work, I study the behaviour of 1,3-benzoxazine-4-one and their thiones with Grignard reagents. Compound (**2**) reacts with Grignard reagents, namely ethyl or phenylmagnesium bromide, to yield 4-(ethyl or phenyl)-1,3 benzothiazin-4-thiol (**5a** and **5b**) respectively. The formation of (5) is explained by the cleavage of C—S bond[4].



The structures of (**5a, 5b**) were proved from the ir spectra which showed absorptions characteristic of ν SH at 2550 cm^{-1} and ν C=N at 1635–1640 cm^{-1}.

^{1}H-NMR spectrum of 5a shows signals at δppm 1.1 (2H, methylene protons), at 0.9 (t.3H, methylproton), at 7.2–7.6 *m*, 8H aromatic protons) and at 4.3 (broad 1H, S*H*).

Also, (**1**) reacts with the same Grignard reagents to yield 2-(*p*-chloro-phenyl)-4-(ethyl, or phenyl)-4-hydroxy-4H-1,3-benzoxazine (6a and 6b) respectively.

The infrared spectra of 6a and 6b exhibits bands at 1640 cm^{-1} due to ν C=N, 3340 cm^{-1} due to ν OH. On the other hand, the benzothiazin derivative[2] was obtained by treating (**2**) with benzylmagnesium chloride, while (**1**) when treated with benzyl chloride under the Grignard reaction conditions gave 2-(*p*-chloro-phenyl)-4-benzylidene 1,3 benzoxazine (**7**).

Compound (**7**) was also obtained unambiguously by fusing compound (**1**) with phenylacetic acid at 160°.

The structure of compound (**7**) was confirmed from the following:

1) Infrared spectrum shows absorption bands at 1610 cm^{-1} (νC=C) and 1625 cm^{-1} (νC=N).

2) ^{1}H-NMR spectrum showed signals at δ ppm 6.3 (*s*, 1H, C=CH), and at 7.3–7.6 (*m*, 13H aromatic protons).

The action of hydrazine hydrate on (**1**) gave the 1,2,4-triazole derivative (**8**), a colourless compound, soluble in aqueous sodium hydroxide solution, giving a violet colour with $FeCl_3$. The ir spectrum of (**8**) shows strong absorption bands at 3350 cm^{-1}, 3260 cm^{-1} and 1635 cm^{-1} attributable to ν OH, ν NH and ν C=N respectively, agreeing well with the proposed structure.

On the other hand, the action of *p*-nitrophenylhydrazine or hydroxylamine on (**1**) led to the formation of *p*-nitrophenylhydrazone and the oxime derivatives (**9a–b**) respectively.

The ir spectra of compound (**9**) exhibit absorption bands at 1632 cm^{-1} and 1620 cm^{-1} attributable to ν of two C=N groups, with additional bands at 3340 cm^{-1}, 3250 cm^{-1} due to ν OH in the case of (**9b**) and ν NH in the case of (**9a**). These ir data are consistent with the suggested structures. Similarly, the thione (**2**) condensed with hydrazine, phenylhydrazine, hydroxylamine and thiosemicarbazide to give the corresponding hydrazone derivatives (**10a–b**), and the oxime and thiosemicarbazone derivatives (**10c–d**) respectively.

The structure of (**10**) was confirmed from its ir spectra which show absorption bands at 1637 cm^{-1}, 1625 cm^{-1} attributable to exo and endo ν C=N groups with additional bands at 3290 cm^{-1} due to ν NH for **10a**, ν of two NH groups at 3250 cm^{-1} and at 1340 cm^{-1} attributable to ν C=S for (**10d**).

EXPERIMENTAL

The ir absorption spectra were determined with a Unicam SP 1200 spectrophotometer in a KBr wafer. The NMR spectra were determined with VN s-60T. Varian. Yields and physical data are shown in table.

(i) Action of phosphorus pentasulphide on benzoxazone (1): formation of (2): A solution of (1) (0.01 mole) and P_2S_5 (0.02 mole) in 100 ml of dry xylene was heated under reflux for 6 hr. The reaction mixture was filtered while hot, and concentrated. The product separated on cooling was crystallized from the proper solvent to give (2). Physical properties and m.p. are given in table.

(iii) Action of amines on thione (2): formation of (**3a–d**): A solution of thione (2) (0.01 mole) and primary amines (0.01 mole), namely, ethylamine, benzylamine, *p*-toluidine and *o*-chloroaniline was heated under reflux for 8 hr. The product that separated on cooling was crystallized from an appropriate solvent to yield 3a–d.

(iii) Action of amines on benzoxazone (1): formation of **4a–d**: A solution of (1) (0.01 mole) and primary amines namely, ethylamine, benzylamine, *p*-methylaniline and *o*-chloroaniline (0.01 mole) in ethanol (50 ml) was heated under reflux for 5 hr. The products that separated on cooling were crystallized from a suitable solvent to give (**4a–d**).

(iv) Action of Grignard reagent on thione (**2**): formation of **5a** and **5b**: A solution of thione **2** (0.01 mole) in dry ether was treated with ethyl-magnesium iodide or phenylmagnesium bromide (0.03 mole) in ether in the course of 30 min. The reaction mixture was heated under reflux for 4 hr., left overnight at room temperature and then decomposed in the usual way. The oil obtained was triturated with light petrol and the products were crystallized from proper solvents to produce **5a** and **5b**.

(v) Action of Grignard reagents on the benzoxazone (**1**): formation of **6a**, **6b** and **7**: A solution of (**1**) (0.01 mole) in dry benzene was treated with an ethereal solution of ethylmagnesium bromide or phenylmagnesium bromide or benzylmagnesium chloride (0.03 mole) for 30 min. The reaction mixture was heated under reflux for 5 hr., left overnight at room temperature and then decomposed in the usual way. The oil obtained was triturated with light petrol and the products were crystallized from the proper solvent.

(vi) Action of phenylacetic acid on benzoxazone (**1**): formation of (7): (1) (0.01 mole) was fused with 0.01 mole phenylacetic acid on an oil bath at 160° for 3 hr. The product obtained was crystallized from alcohol to give (**7**).

(vii) Action of hydrazines on benzoxazone (**1**) or thione (**2**): formation of (**8**), (**9a**) and (**10a** and

TABLE I

Physical data and yields of the compounds prepared

				Analysis %	
Compound	M.P.°C colour	Solvent yield %	Formula (mol. wt.)	Required	Found
2	150	B/P (40–60°)	$C_{14}H_8ClNS_2$	C 58.03	58.01
	orange	60	289.5	H 2.76	2.73
				N 4.84	4.81
				S 22.11	22.10
3a	180	E	$C_{16}H_{13}ClN_2S$	C 63.89	63.86
	yellow	30	300.5	H 4.33	4.30
				N 9.32	9.30
				S 10.65	10.63
3b	135	B	$C_{21}H_{15}ClN_2S$	C 69.52	69.50
	reddish-brown	35	362.5	H 4.14	4.12
				N 7.72	7.70
				S 8.83	8.81
3c	130	B/P	$C_{21}H_{15}ClN_2O$	C 69.52	69.51
	pale-yellow	(40–60°)	362.5	H 4.14	4.13
				N 7.72	7.70
				S 8.83	8.82
3d	165	M	$C_{20}H_{12}Cl_2N_2S$	C 62.66	62.65
	orange	40	383	H 3.13	3.12
				N 7.31	7.31
				S 8.36	8.35
4a	218	B	$C_{16}H_{13}ClN_2O$	C 67.49	67.45
	colourless	60	284.5	H 4.57	4.54
				N 9.84	9.81
4b	165	E	$C_{21}H_{15}ClN_2O$	C 72.73	72.70
	colourless	55	346.5	H 4.33	4.31
				N 8.08	8.07
4c	205	B	$C_{21}H_{15}ClN_2O$	C 72.73	72.70
	colourless	65	346.5	H 4.33	4.31
				N 8.08	8.08
4d	200	M	$C_{20}H_{12}Cl_2N_2O$	C 65.40	65.39
	colourless	80	367	H 3.27	3.26
				N 7.63	7.60
5a	130	P(60–80°)	$C_{16}H_{14}ClNS_2$	C 60.09	60.07
	orange	40	319.5	H 4.38	4.36
				N 4.38	4.37
				S 20.03	20.01
5b	210	B/P(40–60°)	$C_{20}H_{14}ClNS_2$	C 65.34	65.32
	red	50	367.5	H 3.81	3.79
				N 3.81	3.78
				S 17.41	17.39
6a	190	M	$C_{16}H_{14}ClNO_2$	C 66.90	66.89
	colourless	50	287.5	H 4.88	4.87
				N 4.88	4.88

TABLE I

(*contd.*)

Compound	M.P.°C colour	Solvent yield %	Formula (mol. wt.)	Analysis % Required	Analysis % Found
6b	180	B	$C_{20}H_{14}ClNO_2$	C 71.54	71.52
	colourless	40	335.5	H 4.17	4.19
				N 4.17	4.16
7	90	M	$C_{21}H_{14}ClNO$	C 76.02	76.01
	yellow	40	331.5	H 4.22	4.21
				N 4.22	4.22
8	155	M	$C_{14}H_{10}CLN_3O$	C 61.88	61.86
	colourless	50	271.5	H 3.68	3.65
				N 15.47	15.46
9a	210	E	$C_{20}H_{13}CLN_4O_3$	C 61.15	61.13
	orange	60	392.5	H 3.31	3.30
				N 14.27	14.26
9b	200	E	$C_{14}H_9CLN_2O_2$	C 61.65	61.64
	colourless	75	272.5	H 3.30	3.29
				N 10.28	10.26
10a	240	M	$C_{14}H_{10}CLN_3S$	C 58.43	58.40
	pale yellow	50	287.5	H 3.48	3.46
				N 14.61	14.60
				S 11.13	11.12
10b	120	B/P (40–60°)	$C_{20}H_{14}CLN_3S$	C 66.02	66.00
	brown	30	363.5	H 3.85	3.83
				N 11.55	11.54
				S 8.80	8.80
10c	120	B	$C_{14}H_9CLN_2SO$	C 58.23	58.22
	colourless	50	288.5	H 3.12	3.11
				N 9.71	9.70
				S 11.09	11.08
10d	170	M	$C_{15}H_{11}CLN_4S_2$	C 51.95	51.93
	orange	70	346.5	H 3.17	3.16
				N 16.16	16.15
				S 18.47	18.46

B = benzene, E = ethanol, M = methanol, B/P = light petrol

10b). A solution of (**1**) or (**2**) (0.01 mole) and hydrazines namely, hydrazine hydrate, *p*-nitrophenylhydrazine and phenylhydrazine (0.03 mole) in ethanol (50 ml), was refluxed for 8 hr. The solid that separated on cooling was crystallised from a suitable solvent to yield (**8**), (**9a**), (**10a**) and (**10b**).

(viii) Condensation of benzoxazone (**1**) or thione (**2**) with hydroxylamine hydrochloride or thiosemicarbazide: formation of (**9b**), (**10c**) and (**10d**): A mixture of 1 or 2 (0.01 mole) and hydroxylamine hydrochloride or thiosemicarbazide (0.03 mole) in dry pyridine (50 ml) was heated under reflux for 10 hr. The reaction mixture was poured into cold dilute HC I to give solids which were crystallized from a suitable solvent to give (**9b**) and (**10c**) and (**10d**).

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