Asian Journal of Chemistry Vol. 6, No. 3 (1994), 700–702

NOTES

A Simple and Convenient Synthesis of (1, 4)-Benzoxazino-(2, 3 b)-Phenoxazines

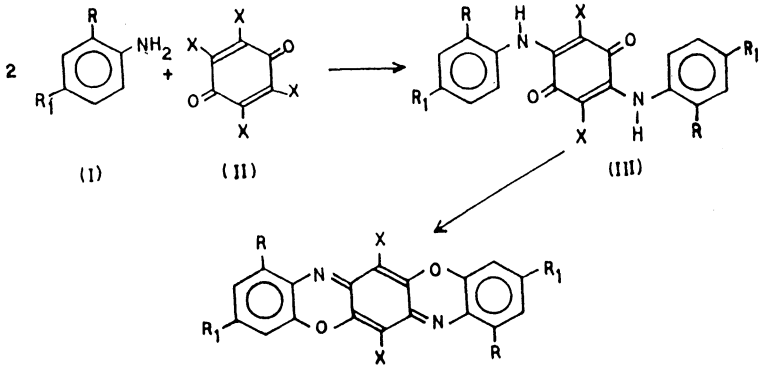
K.G. OJHA*, P. ADWANI, MAHAVEER KAWADIYA and MUKESH TANWAR
Department of Chemistry,
S.D. Government College, Beawar-305 901, India.

Substituted 6, 13-dihalo-(1, 4)-benzoxazino-(2, 3b)-phenoxazines(IV) have been synthesised by condensing arylamines with halogeno-*p*-benzoquinones followed by cyclisation of the resulting diarylamino quinone (III) with benzoyl chloride in nitro benzene.

(1, 4)-Benzoxazino-(2, 3b)-phenoxazines consist of two oxazine rings alternating with three benzene rings. The numerous conjugated double bonds and quinone couplings in a planer structure make them a good chromogenic molecules because of stability and being sparingly soluble in common organic solvents, these are useful for colouring varnishes, plastics, lacquers, viscose, paper and rubber in different shades[1–6]. Their sulphonated derivates have been widely used for dying natural and synthetic fibers in different shades[7, 8].

Keeping the above report in view we under took the synthesis of some hitherto unknown (1, 4)-benzoxazino (2, 3b)-phenoxazines derivatives.

Substituted arylamines (I) 2 mole were condensed with halogeno *p*-benzoquinone(II) (chloranil or bromanil, 1 mole) in ethanolic medium in presence of fused sodium acetate. The resulting diarylamino quinones(III) were cyclised by refluxing with benzoyl chloride in nitrobenzene (Scheme-1).



(I) (II) (III)

(IV)

Cyclisation of III using anhydrous aluminium chloride, conc. sulphuric acid or ferric chloride was also attempted but the reacting yielded only intractable oils from which no pure product could be isolate.

The IR spectra (KBr) of III exhibited bands at 3250–3230 (NH) and 1660–1645 (C=O). The IR spectra of IV show bands in the region 1650—1100 due to C–N and C–C ring vibrations, at 1650–1620 for C = N and at 1250–1100 due to C–C, C–N, C–O rings vibrations of quinoid and aromatic systems. The bands at 1200–1100 cm^{-1} is associated with the asymmetric C–O–C vibrations of oxazine ring.

Bromanil was prepared following the method of Torrey *et al*[9] and was purified by sublimation under reduced pressure. Purity of compounds prepared was tested by TLC on silica gel-G (Merck) in various non-aqueous solvent system. Melting points were determined in open glass capillaries and are uncorrected.

(i) 2,5-Diarylamino-3, 6-dihalo-1, 4-benzoquiones (III a-h)

To the stirred suspension of chloranil or bromanil (0.01 mole), anhydrous sodium acetate (0.05 mole) in ethanol (50 ml) was added an ethanolic solution of arylamine (0.02 mole) when the colour of reaction mixture turned dark. It was heated under reflux for 4 h., filtered hot and the residue washed with hot water and finally with 30% ethanol to give the desired product (Table-1).

TABLE 1
PHYSICAL DATA OF 2,5-DIARYLAMINO-3,6-DIHALO-1, 4-BENZOQUINONES (III a–h)

	Compound			m.p.	Molecular	N*% Found
	R	R_1	X	(°C)	Formula/yield (%)	(Calcd.)
a	CH_3	NO_2	Cl	153	$C_{20}H_{14}Cl_2N_4O_6$ (62)	11.72 (11.74)
b	CH_3	NO_2	Br	219	$C_{20}H_{14}Br_2N_4O_6$ (70)	9.87 (9.89)
c	CH_3	Cl	Cl	173	$C_{20}H_{14}Cl_4N_2O_2$ (75)	6.12 (6.14)
d	CH_3	Cl	Br	238	$C_{20}H_{14}Cl_2Br_2N_2O_2$ (62)	5.11 (5.13)
e	NO_2	CH_3	Cl	267	$C_{20}H_{14}Cl_2N_4O_6$ (70)	11.72 (11.74)
f	NO_2	CH_3	Br	205	$C_{20}H_{14}Br_2N_4O_6$ (70)	9.87 (9.89)
g	OCH_3	NO_2	Cl	170	$C_{20}H_{14}Cl_2N_4O_8$ (75)	10.98 (11.00)
h	OCH_3	NO_2	Br	190	$C_{20}H_{14}Br_2N_4O_8$ (80)	9.33 (9.36)

*All the compounds gave satisfactory C and H analysis

(ii) (1, 4)-Benzoxazino-(2, 3b)-phenoxazines (IV, a-h)

A mixture of III (0.01 mole), nitro benzene (40 ml) and benzoyl chloride (10 ml) was heated under reflux for 4–6 h, cooled and filtered. The residue was washed thoroughly with ethanol followed by water and recrystallised from nitro benzene to give desired product (Table-2).

TABLE 2
PHYSICAL DATA OF (1,4)-BENZOXAZINO
(2,3 b)-PHENOXAZINES (IV a–h)

	Compound (IV)			m.p.(°C)	Molecular Formula/yield (%)	N*% Found (Calcd.)
	R	R_1	X			
a	CH_3	NO_2	Cl	> 360	$C_{20}H_{10}Cl_2N_4O_6$ (65)	11.79 (11.83)
b	CH_3	NO_2	Br	> 360	$C_{20}H_{10}Br_2N_4O_6$ (70)	9.93 (9.96)
c	CH_3	Cl	Cl	> 360	$C_{20}H_{10}Cl_4N_2O_2$ (70)	6.16 (6.19)
d	CH_3	Cl	Br	> 360	$C_{20}H_{10}Cl_2Br_2N_2O_2$ (65)	5.15 (5.17)
e	NO_2	CH_3	Cl	> 360	$C_{20}H_{10}Cl_2N_4O_6$ (70)	11.81 (11.83)
f	NO_2	CH_3	Br	> 360	$C_{20}H_{10}Br_2N_4O_6$ (75)	9.95 (9.96)
g	OCH_3	NO_2	Cl	> 360	$C_{20}H_{10}Cl_2N_4O_8$ (65)	11.03 (11.08)
h	OCH_3	NO_2	Br	> 360	$C_{20}H_{10}Br_2N_4O_8$ (60)	9.38 (9.42)

*All the compounds gave satisfactory C and H analysis

ACKNOWLEDGEMENTS

We are thankful to the Principal & Head of the department for providing facilities. Financial support from UGC, New Delhi is greatfully acknowledged.

REFERENCES

1. K. Vankataraman (Ed.), The Chemistry of Synthetic Dycs., Vol. 2, Chapter XXV pp. 761, Academic Press Inc., New York (1952).
2. H.A. Lubs (Ed.), The Chemistry of Synthetic Dyed and Pigments, Reinhold Pub. Cor., New York (1955).
3. H. Jaeger, Eur. Pat. 141996 (1985); *Chem. Abstr.*, **103**, 10032 (1985).
4. CIBA Ltd., US Pat. 2763641 (1956), *Chem. Abstr.*, **51**, 3153 b (1957).
5. K. Seitz, Eur. Pat. 260277; *Chem. Abstr*, **109**, 56575 (1989).
6. Lauk Urs, (Ciba-Geigy A-G) Eur. Pat. 4861429 (1992), *Chem. Abstr*, **105**, 25819 (1986).
7. K.V. Solodova, M.S. Yaskova, L.K. Trento and N.E. Nozarora; *Zh. Prikl Khim*, **59**, 396 (1986); *Chem. Abstr.*, **105**, 25819 (1986).
8. W. Harms, H. Wolfgang and K. Josef, Eur. Pat. 229, 328, *Chem. Abstr.*, **111**, 8891 (1989).
9. H.A. Torrey and W.H. Hunter, *J. Am. Chem. Soc.*, **34**, 702 (1912).

(*Received*: 21 July 1993; *Accepted*: 14 October 1993) AJC-723