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A Convenient Synthesis of 1,2,4-Trihalophenothiazine-3-ones and Their Conversion into (1,4)–Benzothiazino-(2,3-b)-Phenothiazines

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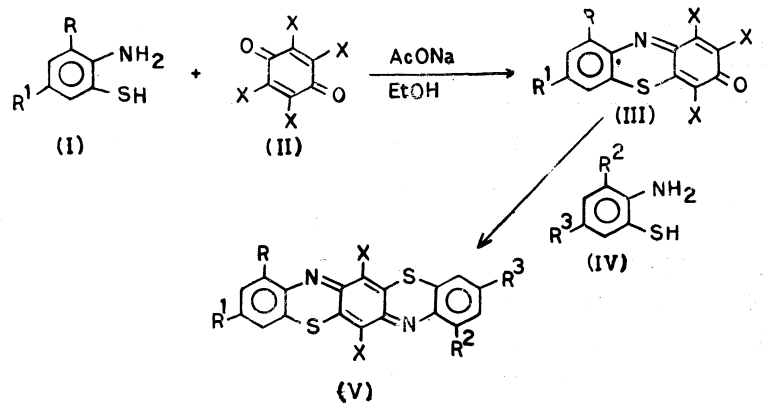
A simple synthesis is reported for (1, 4)-benzothiazino (2, 3-b)-phenothiazines. 2-amino-3-(methoxy/nitro)-5-(nitro/methyl) benzenethiols were condensed with chloranil/bromanil and the resulting phenothiazine-3-ones were further condensed with same or different -amino-benzenethiols to get substituted (1,4)-benzothiazino-(2,3-b)-phenothiazines. Symmetric (1,4)-benzothiazino-(2,3-b)-phenothiazines were also prepared by single step reaction involving condensation of substituted 2-aminobenzenethiols with chloranil/bromanil in 2 : 1 molar ratio. Their spectral studies are also included.

INTRODUCTION

In continuation to our work on 1,4-benzothiazines[1,2] and phenothiazines[3], we are reporting the synthesis of some new 1,4-benzothiazino-(2,3-b)-phenothiazines. 1,4-Benzothiazino-(2,3-b)-phenothiazines are excellent chromogenic molecules and have been used as dye stuffs for cotton and other material such as paper, rubber, plastics and lacquers in different shades[4–7].

Substituted 2-aminobenzenethiols (1,2-amino-3-methoxy-5-nitrobenzenethiol/2-amino-5-methyl-3-nitrobenzenethiol) were condensed with chloranil/bromanil(II) in ethanol in presence of anhydrous sodium acetate to get phenothiazine-3-ones(III). Compounds(III) were further condensed with same or different 2-aminobenzenethiols(IV) in order to obtain substituted (1,4)-benzothiazino-(2,3-b)-phenothiazines(V) (Scheme 1).



Scheme 1

Symmetric compounds(V) were also prepared by an alternative single step reaction. (Scheme 2)

$$\underset{(0.02\ \text{mole})}{\text{I}} + \underset{(0.01\ \text{mole})}{\text{II}} \xrightarrow[\text{EtOH}]{\text{AcONa}} \text{V}$$

Scheme 2

o-Aminothiophenols (I, 0.02 mole) were condensed with halogeno-p-benzoquinones (II, 0.01 mole). The products obtained were identified by mixed melting point, TLC, spectral data and elemental analysis.

EXPERIMENTAL

All the melting points are uncorrected, IR spectra were recorded on Perkin Elmer-781 on KBr pellets. The purity of compounds was checked by TLC on silica gel in various non-aqueous solvent systems. 2-Aminobenzenethiols were prepared by the method reported elsewhere[8]. Bromanil was prepared by the method of Torry and Hunter[9].

(i) Preparation of 1, 2, 4-Trihalophenothiazine-3-ones (III)

To a stirred suspension of chloranil/bromanil (II, 0.01 mole) in ethanol (25 ml) was added substituted 2-aminobenzenethiol (I, 0.01 mole) in ethanol (10 ml) and anhydrous sodium acetate (0.05 mole). The reaction mixture was refluxed for 6 hrs. After cooling at room temperature the solid separated was filtered, washed with water and finally with 30% ethanol. Compounds were crystallised from benzene solution (Table 1)

TABLE 1

PHYSICAL DATA OF 1, 2, 4-TRIHALOPHENOTHIAZINE-3-ONE (III)

Compound III			M.Pt. °C	Yield %	Molecular Formula	N% (Found)	N% (Calcd.)
R	R_1	X					
H	H	Cl	104	62	$C_{12}H_4NSOCl_3$	4.39	4.42
H	H	Br	137	53	$C_{12}H_4NSOBr_3$	3.10	3.11
NO_2	CH_3	Cl	110	57	$C_{13}H_5N_2SO_3Cl_3$	7.41	7.45
NO_2	CH_3	Br	167	45	$C_{13}H_5N_2SO_3Br_3$	5.49	5.50
OCH_3	NO_2	Cl	167	48	$C_{13}H_5N_2SO_4Cl_3$	7.16	7.15
OCH_3	NO_2	Br	165	50	$C_{13}H_5N_2SO_4Br_3$	5.31	5.33

(ii) Prepration of (1, 4)-benzothiazino (2, 3-b)-phenothiazines

To a mixture of III (0.01 mole) and substituted 2-aminobenzenethiol IV (0.01 mole) in ethanol (20 ml) was added anhydrous sodium acetate. The mixture was refluxed for 6 hrs and the product was worked up as described above (Table 2).

TABLE 2

PHYSICAL DATA OF (1, 4) BENZOTHIAZINO-(2, 3-b)-PHENOTHIAZINES (V)

Compound V					M. pt. °C	Yield %	Molecular Formula	N% (Found)	N% Calcd.
R	R_1	R_2	R_3	X					
H	H	NO_2	CH_3	Cl	187	43	$C_{19}H_9N_3S_2O_2Cl_2$	9.39	9.41
H	H	NO_2	CH_3	Br	192	51	$C_{19}H_9N_3S_2O_2Br_2$	7.82	7.85
H	H	OCH_3	NO_2	Cl	194	57	$C_{19}H_9N_3S_2O_3Cl_2$	9.06	7.09
H	H	OCH_3	NO_2	Br	203	63	$C_{19}H_9N_3S_2O_3Br_2$	7.60	7.62
NO_2	CH_3	NO_2	CH_3	Cl	180	49	$C_{20}H_{10}N_4S_2O_4Cl_2$	11.06	11.08
NO_2	CH_3	NO_2	CH_3	Br	210	53	$C_{20}H_{10}N_4S_2O_4Br_2$	9.39	9.42
OCH_3	NO_2	OCH_3	NO_2	Cl	227	47	$C_{20}H_{10}N_4S_2O_6Cl_2$	10.41	10.42
OCH_3	NO_2	OCH_3	NO_2	Br	183	69	$C_{20}H_{10}N_4S_2O_6Br_2$	8.91	8.94

IR Spectra

The IR spectra of phenothiazone III exihibit a strong band in the region 1600-1620 cm^{-1} due to C=O stretching vibration and band at 1560-1590 cm^{-1} are due to C=N vibration. The IR spectra of all these 1, 4-benzothiazino-(2, 3-b)-phenothiazines also show a number of sharp and medium bands in the region 1600-1200 cm^{-1} which can be assigned to C—C, C—N ring vibrations.

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CORRIGENDUM

Paper entitled, "Studies on Complex Arylhydrazones, Part VI" [Asian J. Chem., Vol. 4, No. 3, 652-654 (1992)].

In structure I, please substitute:

X = H	referred as HL_1
X = *p*-NO_3	referred as HL_2
X = *o*-Me	referred as HL_3
X = *p*-Me	referred as HL_4
X = *p*-Br	referred as HL_5