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Organic Chemistry

SYNTHESIS OF NAPHTH[2,3-d]IMIDAZO[2′,3′-b]-THIADIAZOLO-5,10-DIONES

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A series of 2-chloro-3-thiadiazolylamino-1,4-naphthoquinones (II) has been synthesised by condensing 2,3-dichloro-1,4-naphthoquinone with 5-alkyl-2-amino-1,3,4-thiadiazoles (II). Cyclization of the compound in glacial acetic acid gave Naphth[2,3-d]imidazo[2′,3′-b]thiadiazolo-5,10-diones (III).

Keywords: **Naphth[2,3-d]imidazo[2′,3′-b]thiadiazolo-5,10 diones; 2,3-dichloro-1,4-naphthoquinone; 5-alkyl-2-amino-1,3,4-thiadiazoles**

INTRODUCTION

NAPHTHOQUINONES are useful inhibitors of acid formation by oral bacteria from carbohydrates (Fosdick *et al.*, 1942; and Calandra *et al.*, 1944). Buu-Hoi (1944) reported that certain arylamine derivatives of 1,4-naphthoquinone are capable of inhibiting the growth of tubercle *Bacillus*. Calandra *et al.* (1944) prepared some amino derivatives of 2-chloro-1,4-naphthoquinone of four types: aminopyridine, sulphonamides, aminoalkanes and amino acids and found all of them as very active inhibitors of acid production by oral bacteria.

A perusal of literature reveals that no work has been done on the reaction of 5-alkyl-2-amino-1,3,4-thiadiazole with 2,3-dichloro-1,4-naphthoquinone.

In continuation of our work on thiadiazolobenzimidazoles (Soni & Saxena, 1979), the present communication describes the synthesis of some new (*i*) 2-chloro-3-thiadiazolylamino-1,4-naphthoquinone (Table I), (*ii*) naphth[2,3-d]imidazo[2′,3′-b]thiadiazolo-5,10-diones (Table II).

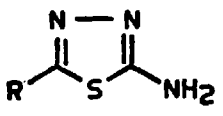
5-alkyl-2-amino-1,3,4-thiadiazoles (I) were reacted with 2,3-dichloronaphthoquinone in ethanol to give the corresponding thiadiazolylamino quinones (II). II could be cyclized to the corresponding quinones (III), when refluxed in glacial acetic acid. The preliminary screening of II shows that some of them possess antitubercular activity.

IR spectra of the intermediate 2-chloro-3-thiadiazolylamino-1,4-naphthoquinones (II) showed characteristic γN-H at 3250-3450 cm^{-1}, which were absent in the spectra of cyclized products. The bands corresponding to γC=O in conjugation with NH substituent were observed in the region 1660–1675 cm^{-1}. The band in the region 1625–1650 cm^{-1} were assigned to non-conjugated γC=O. This is in contrast to the γC=O in the cyclized products appearing at higher frequency (~1680 cm^{-1}) as a

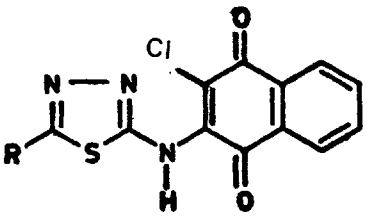
TABLE I

2-Chloro-3-thiadiazolylamino-1,4-naphthoquinones (II)

Compd. No.	R	Mol. Formula	M.P. °C	% Analysis Calcd.	% Analysis Found	Yield %	UV spectra Ethanol λ_{max} nm	UV spectra Ethanol log ε
1.	H	$C_8H_4N_3O_2SCl$	241–42	C, 39.7	39.5	41	251	3.91
				H, 1.6	1.4		354	3.85
				N, 17.3	17.1		552	4.21
2.	CH_3	$C_9H_6N_3O_2SCl$	194	C, 42.2	42.1	37	249	3.87
				H, 1.1	1.1		352	3.89
				N, 16.4	16.2		541	4.17
3.	C_2H_5	$C_{10}H_8N_3O_2SCl$	207	C, 44.5	44.3	46	255	3.85
				H, 2.9	2.9		353	3.91
				N, 15.5	15.3		537	4.26
4.	$CH_3(CH_2)_2$	$C_{11}H_{10}N_3O_2SCl$	187	C, 46.5	46.1	35	247	3.93
				H, 3.5	3.4		358	3.81
				N, 14.0	14.0		547	4.15
5.	$(CH_3)_2CH$	$C_{11}H_{10}N_3O_2SCl$	178	C, 46.5	46.2	33	257	4.05
				H, 3.5	3.1		348	3.76
				N, 14.0	13.8		525	4.11



(I)



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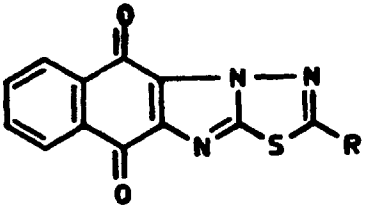

(III)

split band thus supporting the cyclic structure. The γC—Cl bands appeared as medium to strong bands in the region 710–720 cm^{-1}.

The UV spectra of II and III were recorded in ethanol (Tables I and II).

TABLE II

Naphth[2,3-d]imidazo[2',3'-b]thiadiazolo-5,10-diones (III)

Compd. No.	R	Mol. Formula	M.P. °C	% Analysis		Yield %	UV spectra	
				Calcd.	Found		Ethanol	
							λ_{max} nm	log ε
1.	H	$C_8H_3N_3O_2S$	156	C, 46.8	46.6	34	257	4.31
				H, 1.4	1.3		316	4.15
				N, 20.4	20.2		455	3.85
2.	CH_3	$C_9H_5N_3O_2S$	174	C, 49.3	49.1	31	251	4.17
				H, 2.2	2.2		329	4.07
				N, 19.1	19.0		461	3.77
3.	C_2H_5	$C_{10}H_7N_3O_2S$	196	C, 51.5	51.2	37	255	4.37
				H, 3.0	2.9		315	4.01
				N, 18.0	17.7		459	4.03
4.	$CH_3(CH_2)_2$	$C_{11}H_9N_3O_2S$	207	C, 53.4	53.1	35	252	4.15
				H, 3.6	3.4		342	4.09
				N, 17.0	16.7		451	3.91
5.	$(CH_3)_2CH$	$C_{11}H_9N_3O_2S$	254	C, 53.4	53.2	24	259	4.27
				H, 3.6	3.3		315	4.12
				N, 17.0	17.0		457	3.91

EXPERIMENTAL

All the reagents were thoroughly dried and purified before use. All the melting points were determined on Kofler instrument and were uncorrected. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. in KBr. UV absorption spectra were scanned in Beckman Spectrophotometer Model DU-2.

5-Alkyl-2-amino-1,3,4-Thiadiazoles

These were prepared by known method (Japan Patent, 1967)

2-Chloro-3-Thiadiazolylamino-1,4-Naphthoquinone (II)

A mixture of 5-alkyl-2-amino-1,3,4-thiadiazole (0.01 mol), and 2,3-dichloro-1,4-naphthoquinone in 50ml ethanol and 1.5ml diethylaniline was refluxed for 24hrs. The reaction mixture was then concentrated. The desired product separated on cooling was filtered off at the pump. The product was recrystallised from an appropriate solvent. The yields, m.p. etc., are given in Table I.

Cyclization of 2-Chloro-3-Thiadiazolylamino-1,4-Napthhoquinones (II)

Formation of naphth[2,3-d]imidazo[2',3'-b]thiadiazolo-5,10-diones—A solution of II (0.5 g) in glacial acetic acid (30ml) was heated under reflux for 30 min. The

mixture was concentrated and cooled, when the cyclized product (III) was separated. It was recrystallised from ethanol. The yields, m.p., etc. are given in Table II.

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