SYNTHESIS OF SOME NEW TYPE OF NAPHTHOTHIAZOLE TRIAZOLES FROM LAWSONE

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A series of 3-aryl naphtho[2',3':4,5]thiazolo[3,2-*b*]-1,2,4-triazolo-5,10-diones (*V*) have been prepared by the condensation of bromo lawsone (*I*) with 5-mercapto-3-substituted 1,2,4-triazole (*II*) followed by cyclization of the resulting uncyclized products (*IV*) with alcohol and sulfuric acid. The products are identical with the condensation products of 2,3-dichloro naphthoquinone (*III*) with 5-mercapto-3-substituted 1,2,4-triazoles in the presence of anhydrous alcohol containing fused sodium acetate.

In continuation of our earlier work on the synthesis of heterocyclic systems derived from natural quinones[1-3], we are now reporting the preparation of a novel heterocyclic system, namely 3-aryl/heteroaryl naphtho[2',3':4,5]thiazolo[3,2-*b*]triazolo-5,10-dione (*V*) in a two step process starting from bromo lawsone (*I*) in good yield.

The reaction of bromo lawsone with 3-substituted 1,2,4-triazoles in anhydrous alcohol or in acetic led to the formation of 2-hydroxy-3-[(5-aryl-1,2,4-triazol-3-yl)thio]1,4-naphthoquinone (*IV*). In this reaction the more nucleophilic thiol group attacks the vinyl carbon displacing the bromine to give *IV*. The structures of these compounds were established by chemical (positive ferric chloride test), microanalytical and spectral data. Subsequently these compounds were cyclized by refluxing them in a mixture of alcohol and sulfuric acid (4 : 1) to afford the title compounds (*V*). These compounds are also obtained directly from 2,3-dichloro naphthoquinone (*III*) and *II* in absolute alcohol containing fused sodium acetate.

EXPERIMENTAL

Lawsone was extracted from the fresh leaves of *Lawsonia intermis*. Bromo lawsone was prepared according to our earlier procedure[3], 3-aryl/heteroaryl 5-mercapto-1,2,4-triazoles were prepared as described in literature[4,5]. NMR spectra were recorded (in $CDCl_3$) on 60 MHz Varian spectrometer using TMS as

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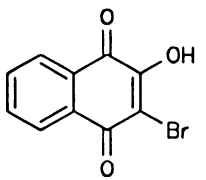
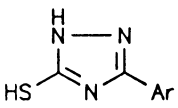
internal standard, chemical shifts are given in ppm (δ-scale). IR spectra were recorded in KBr pellets (wavenumbers in cm^{-1}).

Preparation of 2-Hydroxy-3-[[(5-aryl/heteroaryl)-1,2,4-triazol-3-yl]thio]-1,4-naphthoquinones (*IV*); General Procedure

A mixture of bromo lawsone (*I*) (0.01 mol) and 5-mercapto-3-substituted 1,2,4-triazole (*II*) (0.01 mol) was taken in absolute alcohol and refluxed for 3 – 4 h. The reaction mixture was cooled, the solid separated was filtered and crystallized from suitable solvents. Physico-chemical data of compounds *IV* are given in Table I. IR spectrum of *IVa*: 1 640 and (1 650) (C=O quinone) and 3 300 – 3 100 (OH), ^1H NMR spectrum of *IVa*: 6.43 s, 1 H (NH); 7.4 – 7.6 m, 4 H (aromatic); 7.8 – 8.2 m, 5 H (aromatic). Mass spectrum of *IVa* (*m/z*): 349 (M^+, 100), 331 (9.5), 174 (20), 146 (5.5), 118 (29.8), 104 (46.3) and 77 (33). IR spectrum of *IVb*: 1 655 – 1 640 (C=O), 3 300 – 3 150 (OH). ^1H NMR spectrum of *IVb*: 6.50 s, 1 H (NH); 2.6 s, 3 H (CH_3); 7.3 – 8.3 m, 8 H (aromatic).



I



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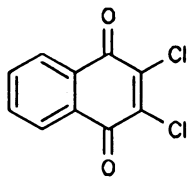

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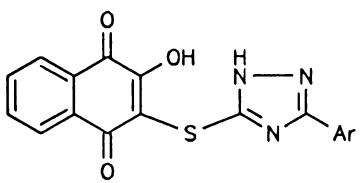
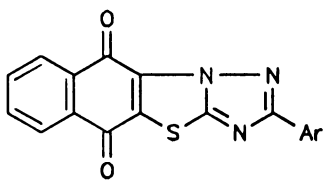


IV



V

In formulae *II*, *IV*, *V* : *a*, Ar = C_6H_5
b, Ar = *p*-$CH_3C_6H_4$
c, Ar = *m*-$CH_3C_6H_4$
d, Ar = *p*-$CH_3OC_6H_4$
e, Ar = *p*-$O_2NC_6H_4$
f, Ar = *m*-$O_2NC_6H_4$
g, Ar = *p*-ClC_6H_4
h, Ar = *o*-ClC_6H_4

TABLE I

Physical data of 2-hydroxy-3-[(5-aryl-1,2,4-triazol-3-yl)thio]-1,4-naphthoquinones *IV* and 3-aryl naphtho-[2′3′:4,5]thiazolo[3,2-*b*]-1,2,4-triazolo-5,10-diones *V*

Compound	Formula (M. w.)	M. p. °C	Calculated/Found			
			% C	% H	% N	% S
IVa	$C_{18}H_{11}N_3O_3S$ (349)	248 – 250[a]	61.89 61.85	3.15 3.10	12.03 12.00	9.17 9.12
IVb	$C_{19}H_{13}N_3O_3S$ (363)	236 – 238[a]	62.81 62.80	3.58 3.55	11.57 11.55	8.81 8.76
IVc	$C_{19}H_{13}N_3O_3S$ (363)	169 – 171[a]	62.81 62.79	3.58 3.58	11.57 11.50	8.81 8.80
IVd	$C_{19}H_{13}N_3O_4S$ (379)	269 – 270[a]	60.16 60.00	3.43 3.42	11.08 11.00	8.44 8.40
IVe	$C_{18}H_{10}N_4O_5S$ (394)	196 – 198[a]	54.82 54.80	2.54 2.51	14.21 14.20	8.12 8.22
IVf	$C_{18}H_{10}N_4O_5S$ (394)	250 – 252[a]	54.82 54.79	2.54 2.52	14.21 14.21	8.12 8.11
IVg	$C_{18}H_{10}N_3O_3ClS$ (383.5)	261 – 263[a]	56.32 56.25	2.61 2.60	10.95 10.90	8.34 8.31
IVh	$C_{18}H_{10}N_3O_3ClS$ (383.5)	223 – 225[a]	56.32 56.28	2.61 2.56	10.95 10.90	8.34 8.31
Va	$C_{18}H_9N_3O_2S$ (331)	301 – 303[b]	65.26 65.22	2.72 2.70	12.69 12.65	9.67 9.67
Vb	$C_{19}H_{11}N_3O_2S$ (345)	243 – 245[b]	66.09 66.00	3.19 3.00	12.17 12.10	9.27 9.21
Vc	$C_{19}H_{11}N_3O_2S$ (345)	252 – 253[b]	66.09 66.11	3.19 3.00	12.17 12.15	9.27 9.20
Vd	$C_{19}H_{11}N_3O_3S$ (361)	273 – 275[b]	66.16 66.19	3.05 3.04	11.63 11.60	8.86 8.78
Ve	$C_{18}H_8N_4O_4S$ (376)	311 – 313[b]	57.45 57.60	2.13 2.10	14.89 14.81	8.51 8.51
Vf	$C_{18}H_8N_4O_4S$ (376)	304 – 306[b]	57.45 57.50	2.13 2.00	14.89 14.82	8.51 8.50
Vg	$C_{18}H_8N_3O_2ClS$ (365.5)	283 – 285[b]	59.10 59.00	2.19 2.12	11.49 11.45	8.75 8.71
Vh	$C_{18}H_8N_3O_2ClS$ (365.5)	261 – 262[b]	59.10 59.00	2.19 2.11	11.49 11.42	8.75 8.72

[a] Recrystallized from ethanol; [b] purified on column using chloroform as eluent. Compounds *IVa – IVh* were obtained in 80 – 90% yield. Compounds *Va – Vb* were obtained in 60 – 70% yield.

Preparation of *V* Starting from *IV*; General Procedure

Uncyclized product *IV* (0.01 mol) was dissolved in 30 ml of alcohol and 7 ml of concentrated H_2SO_4 was added dropwise while stirring the reaction mixture. The reaction mixture was refluxed on water bath for 6 h. The reaction mixture was cooled and poured over crushed ice. The solid thus separated was filtered and purified on wet column using chloroform eluent. Physico-chemical data of compounds *V* are given in Table I. IR spectrum of *Va*: 1 650 and 1 640 (quinonoid C=O). ^{1}H NMR spectrum of *Va*: 6.9 – 8.5 m, 9 H (aromatic). Mass spectrum of *Va* showed the molecular ion peak at *m/z* 331 (M^+, 100). IR spectrum of *Vb*: 1 660 – 1 650 (C=O). ^{1}H NMR spectrum of *Vb*: 2.50 s, 3 H (CH_3); 7.0 – 8.8 m, 8 H (aromatic).

Preparation of 3-Aryl Naphtho[2',3':4,5]thiazolo[3,2-*b*]-1,2,4-triazolo-5,10-diones (*V*) from 2,3-Dichloronaphthoquinone (*II*); General Procedure

A mixture of 2,3-dichloronaphthoquinone (0.01 mol) and appropriate 5-mercapto-3-substituted 1,2,4-triazole (*III*) (0.01 mol) and anhydrous sodium acetate (0.01 mol) in anhydrous ethanol (20 ml) was refluxed for 6 h on steam bath. The reaction mixture was cooled and the solid thus separated was washed with water and recrystallized from suitable solvents. The compounds were found to be identical with those prepared by methods mentioned above (mixed m.p., TLC, IR spectra).

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