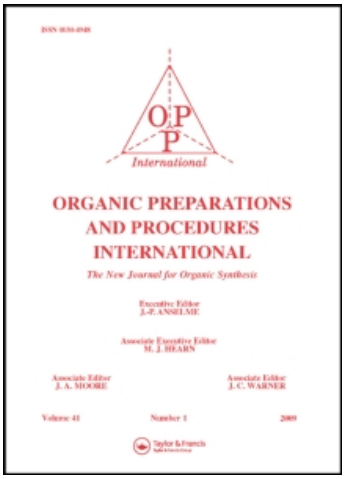

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PHOTOHALOGENATION OF LAWSONE AND PREPARATION OF 3-SUBSTITUTED 5H-NAPHTHO-[2,3-e]-s-TRIAZOLO[3,4-b][1,3,4]THIADIAZINE-6,11-DIONE

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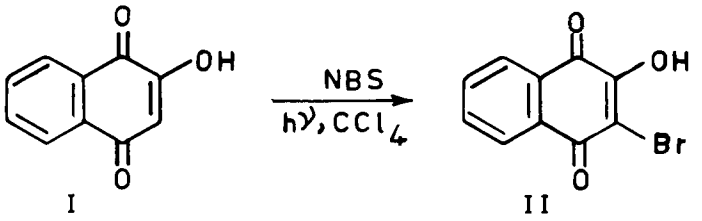
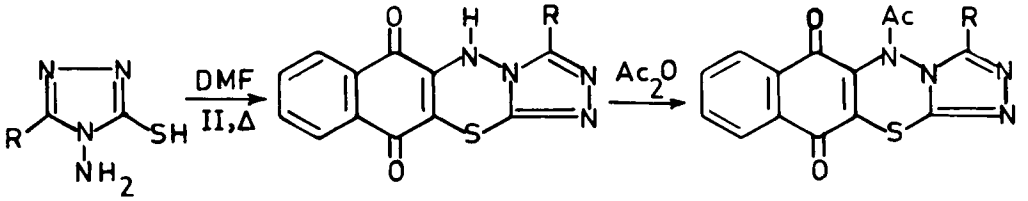
As a continuation of our earlier work on heterocyclic systems from natural quinones,[1] we are now reporting the preparation of a novel heterocyclic system, namely 3-(substituted)-5H-naphtho[2,3-e]-s-triazolo-[3,4-b][1,3,4]thiadiazine-6,11-dione (IV) in a single step from bromolawsone (II) which has been obtained by a novel procedure from lawsone in excellent yields. Lawsone (I, extracted from Lawsonia alba) was halogenated photochemically (300W tungsten lamp) in dry carbon tetrachloride with N-bromosuccinimide using benzoyl peroxide as radical initiator to give II in 93% yield. The structure of this compound was es-



I II



III IV V

tablished from analytical and spectral data. The absence of the characteristic vinylic proton of quinone ring at δ 5.96 in the ^1H NMR spectrum of II confirms bromination at the vinylic carbon atom; this is

further confirmed in the mass spectrum by the presence of an M+2 peak of equal intensity to the M^+ peak which indicates the presence of one bromine atom.

3-Substituted-4-amino-5-mercapto-1,2,4-triazoles (III) were prepared by known procedures[2-4] and treated with bromolawsone (II) in the presence of dimethylformamide to furnish the 3-(substituted)-5H-naphtho[2,3-e]-s-triazolo[3,4-b][1,3,4]thiadiazine-6,11-dione (IV); the reaction may also be carried out in ethanol but the yields were poor. The structures of IV were confirmed by converting these compounds into their N-acetyl derivatives (V); they also failed to react with o-phenylenediamine thus ruling out an o-quinonoid structure. The structure of all the new compounds prepared was confirmed by analytical and spectral data.

EXPERIMENTAL SECTION

All melting points were determined in open capillary tubes using sulphuric acid bath and are uncorrected. IR spectra (ν_{max} cm^{-1}) were recorded in Nujol on Perkin-Elmer-282 instrument. The ^1H NMR spectra were recorded on Varian 90 MHz spectrometer using TMS as internal standard and chemical shifts are expressed in δ ppm. Mass spectra were scanned on a JEOL-JMS-300 spectrometer at 70 eV. Microanalyses were performed at Central Drug Research Institute, Lucknow, India. The purity of the compounds were monitored by TLC, performed on silica gel plates (Merck) and using chloroform-methanol as the eluent. Chemical analysis was done at each stage to confirm the presence or absence of bromine by Bielstein's and Lassaigne's tests. The intactness of 1,4-quinone moiety was tested by reduction with Zn-AcOH and reoxidation on exposure to air. All compounds synthesized were very sensitive towards alkalies.

Bromolawsone (II).- Lawsone (1.74 g, 0.01 mol) in dry carbon tetrachloride (30 ml) and N-bromosuccinimide (1.78 g, 0.01 mol) in the presence of benzoyl peroxide (100 mg) were refluxed on a 300W tungsten lamp for 6 hrs. The reaction mixture was filtered while hot and the solvent was evaporated. The crude product was crystallized from benzene to give (2.35 g, 93%) of lemon yellow crystals, mp. 205°, lit.[5] mp. 202°.

IR (ν_{max}, Nujol): 720(C-Br), 1630, 1645 (quinonoid, C=O), 3100-3250 (broad, -OH).

TABLE 1. Yields, mps and Elemental Analyses

Comp.	R	Yield (%)	mp.[a] (°C)	Elemental Analyses Calcd (Found) C	H	N	S
II	-	93	205	47.43 (47.42)	1.98 (1.99)	-	-
IVa	Methyl	70	>330	54.93 (54.91)	2.82 (2.84)	19.72 (19.73)	11.27 (11.26)
IVb	Ethyl	69	>330	56.37 (56.38)	3.35 (3.35)	18.79 (18.80)	10.74 (10.72)
IVc	Propyl	72	150 (dec.)	57.69 (57.68)	3.84 (3.82)	17.94 (17.97)	10.26 (10.24)
IVd	Phenyl	87	284	62.43 (62.40)	2.89 (2.88)	16.18 (16.16)	9.25 (9.26)
IVe	p-Tolyl	88	290	63.33 (63.32)	3.33 (3.34)	15.55 (15.56)	8.89 (8.89)
IVf	p-Nitro-phenyl	86	160	55.24 (55.22)	2.30 (2.28)	17.90 (17.88)	8.18 (8.19)
IVg	m-Nitro-phenyl	78	>330	55.24 (55.26)	2.30 (2.30)	17.90 (17.88)	8.18 (8.12)
IVh	p-Chloro-phenyl	82	305	56.77 (56.76)	2.36 (2.35)	14.72 (14.76)	8.41 (8.43)
IVi	o-Chloro-phenyl	86	>330	56.77 (56.78)	2.36 (2.36)	14.72 (14.70)	8.41 (8.42)
IVj	Benzyl	87	122	63.33 (63.32)	3.33 (3.32)	15.55 (15.55)	8.89 (8.82)
IVk	4-Pyridyl	82	280	58.79 (58.78)	2.59 (2.60)	20.17 (20.18)	9.22 (9.24)
Va	Methyl	60	328 (dec.)	55.21 (55.22)	3.07 (3.05)	17.18 (17.19)	9.81 (9.80)
Vb	Phenyl	60	261	61.85 (61.84)	3.09 (3.08)	14.43 (14.43)	8.25 (8.21)
Vc	p-Tolyl	62	270	62.69 (62.68)	3.48 (3.47)	13.93 (13.94)	7.96 (7.97)
Vd	p-Chloro-phenyl	58	310	56.80 (56.80)	2.60 (2.58)	13.25 (13.21)	7.57 (7.56)
Ve	o-Chloro-phenyl	56	315	56.80 (56.79)	2.60 (2.61)	13.25 (13.25)	7.57 (7.58)
Vf	4-Pyridyl	60	>330	58.61 (58.60)	2.83 (2.82)	17.99 (17.98)	8.23 (8.21)

a) Compounds IVa-k were crystallized from benzene. b) The N-acetyl derivatives (Va-f) were crystallized from HOAc.

^{1}H NMR(Acetone-d_6): δ 7.20-8.00 (m, 4H, aromatic).

Mass: m/e 253 (M^+, 100), 232(30), 228(30), 176(76), 145(35), 117(30), 105(54).

3-(Substituted)-5H-naphtho[2,3-e]-s-triazolo[3,4-b][1,3,4]thiadiazine-6,11-dione (IV). General Procedure.- A mixture of bromolawsone (2.53 g, 0.01 mol) and the appropriate 3-substituted-4-amino-5-mercapto-1,2,4-triazole (0.01 mol) was stirred mechanically in hot DMF (40 ml) at 85-90° for a period of 5 hrs. The reaction mixture was cooled, the solid which separated was collected and crystallized from suitable solvents (see Table 1).

TABLE 2. Spectral Data of Compounds IV and V

Comp.	R	^{1}H NMR (ppm) NH[c]	Ar-H	Other	IR NH	C=O (quinone)	C=O (N-acetyl)
IVd[a,d]	Phenyl	3.7	7.2-7.6	-	3250	1620 1600	-
IVe[a]	p-Tolyl	3.8	7.3-7.6	2.1(CH_3)	3240	1615 1600	-
IVh[a]	p-Chloro-phenyl	3.8	7.2-7.7	-	3250	1620 1605	-
Vc[a]	p-Tolyl	-	7.2-7.7	2.10($NCOCH_3$) 2.22(CH_3)	-	1640	1780
Vd[b]	p-Chloro-phenyl	-	7.4-7.8	2.04($NCOCH_3$)	-	1645	1780

a) NMR spectra of all the compounds were recorded in $CDCl_3$.

b) NMR spectrum was recorded in a mixture of $CDCl_3$ and DMSO-d_6.

c) These protons disappeared on shaking with D_2O.

d) Mass spectrum of compound IVd: m/e = 346(M^+.100), 277(15), 160(40), 132(40), 130(15), 104(26), 103(26), 89(35).

Preparation of N-Acetyl Derivatives of IV. General Procedure.- N-Acetyl derivatives of IV were prepared by dissolving these compounds in minimum amount of hot acetic anhydride and keeping the reaction mixture at room temperature for 24 hrs. in the presence of catalytic amounts of pyridine. The reaction mixture was then digested with cold water. The resulting solids were collected and crystallized. The analytical and spectral data of the compounds II, IV and V are collected in the Tables 1 and 2 respectively.

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