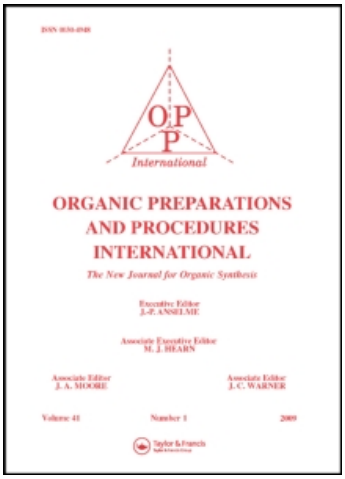

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

PREPARATION OF NOVEL 2-ARYL-4H-NAPHTH[2,1-e]-1,3,4-OXADIAZINE- 6-OL DERIVATIVES

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To cite this Article Kumar, R. Ashok , Kokate, C. K. , Rao, M. S. and Rao, T. V. Padmanabha(1989) 'PREPARATION OF NOVEL 2-ARYL-4H-NAPHTH[2,1-e]-1,3,4-OXADIAZINE- 6-OL DERIVATIVES', Organic Preparations and Procedures International, 21: 3, 380 — 383
To link to this Article: DOI: 10.1080/00304948909356406
URL: http://dx.doi.org/10.1080/00304948909356406

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3. The sterochemistry of this ketone was established by direct comparison with an authentic sample prepared by ring expansion[2d] of (±)-1,2,3,4,4aα,9,10,10a-octahydro-7-methoxy-2α -methyl-11-oxo-2β, 10aβ-ethanophenanthrene [P. N. Chakrabortty, R. Dasgupta, S. R. Ghosh and U. R. Ghatak, Tetrahedron, 28, 4653 (1972)].

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PREPARATION OF NOVEL

2-ARYL-4H-NAPHTH[2,1-e]-1,3,4-OXADIAZINE- 6-OL DERIVATIVES

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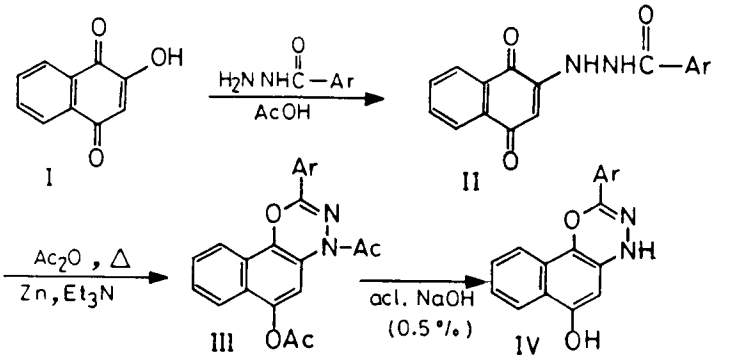
As a continuation of our earlier work on heterocyclic systems from natural quinones,[1-4] we are now reporting the preparation of novel heterocyclic system namely 2-aryl-4H-naphth[2,1-e]-1,3,4-oxadiazine-6-ol (IV) in a three-step process from Lawsone, a natural quinone, in good yields. Lawsone (I, extracted from Lawsonia alba) was first treated in acetic acid with aroylhydrazines to give 2-aroyl-hydrazino-1,4-napthoquinone (II) in excellent yields.



As the attempts for direct cyclization of II to give the title products failed under various

TABLE 1. Yields, mps and Elemental Analyses

Comp.	R	Yield (%)	m.p. (°C)	Elemental Analyses Calcd (Found) C	H	N
IIa	Phenyl	72	210 a	69.86 (69.62)	4.10 (4.00)	9.58 (9.52)
IIb	p-Tolyl	60	243 a	66.66 (66.60)	4.57 (4.39)	9.15 (9.10)
IIc	p-Nitrophenyl	68	235 b	57.14 (57.05)	3.08 (3.10)	14.56 (14.52)
IId	p-Methoxyphenyl	62	218 a	65.66 (65.60)	4.21 (4.20)	8.43 (8.42)
IIe	p-Chlorophenyl	60	228 b	62.57 (62.55)	3.27 (3.19)	8.58 (8.60)
IIf	p-Hydroxyphenyl	60	200 b	66.23 (66.20)	3.89 (3.88)	9.09 (9.00)
IIIa	Phenyl	81	206 b	70.00 (70.00)	4.44 (4.43)	7.77 (7.59)
IIIb	p-Tolyl	75	213 b	70.58 (70.38)	4.81 (4.82)	7.48 (7.42)
IIIc	p-Nitrophenyl	68	216 c	62.22 (61.18)	3.70 (3.59)	10.35 (10.37)
IIId	p-Methoxyphenyl	70	225 b	66.66 (66.42)	4.61 (4.55)	7.15 (7.17)
IIIe	p-Chlorophenyl	65	206 c	63.95 (63.89)	3.80 (3.72)	7.10 (7.10)
IIIf	p-Hydroxyphenyl	63	202 b	67.20 (67.19)	4.00 (4.06)	7.45 (7.46)
IVa	Phenyl	87	230 a	73.91 (73.80)	4.34 (4.28)	10.15 (10.14)
IVb	p-Tolyl	82	223 a	74.48 (74.40)	4.82 (4.69)	9.66 (9.65)
IVc	p-Nitrophenyl	80	240 d	63.55 (63.52)	3.42 (3.40)	13.05 (13.08)
IVd	p-Methoxyphenyl	79	225 a	70.35 (70.19)	4.56 (4.60)	9.10 (9.12)
IVe	p-Chlorophenyl	75	242 e	65.80 (65.76)	3.54 (3.60)	9.00 (9.03)
IVf	p-Hydroxyphenyl	72	213 a	68.91 (68.92)	4.05 (4.00)	9.45 (9.45)

a) Crystallized from benzene. b) Crystallized from methanol. c) Crystallized from ethanol. d) Crystallized from pet. ether (60-80°). e) Crystallized from benzene-pet. ether (60-80°).

conditions, compound II was first subjected to reductive cyclization in acetic anhydride to give 4-acetyl-2-aryl-4H-naphth[2,1-e]-1,3,4-oxadiazine-6-ol acetate (III). Finally, 2-aryl-4H-naphth-[2, 1-e]-1,3,4-oxadiazine-6-ol (IV) was prepared by the deacetylation of III. The structure of all the new compounds prepared was confirmed by analytical and spectral data.

EXPERIMENTAL SECTION

All mps. were determined in open capillary tubes using sulphuric acid bath and are uncorrected. IR spectra (cm^{-1}) were recorded in Nujol on a Perkin-Elmer-282 instrument. The ^1H NMR spectra were recorded on a Varian 90 MHz spectrometer using TMS as internal standard; chemical shifts are expressed in 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 was monitored by TLC, performed on silica gel plates (Merck) and using chloroform-methanol (9:1) as the eluent. Chemical analysis was done at each stage to confirm the presence or absence of 1,4-quinone moiety by reduction with Zn-AcOH and reoxidation on exposure to air.

2-Aroylhydrazino-1,4-naphthoquinone (II). General Procedure.- A mixture of Lawsone (1.74 g, 0.01 mol) and the appropriate aroyl hydrazine (0.01 mol) was refluxed on a steam bath for a period of 3-4 hr. The reaction mixture was cooled and poured over crushed ice. The solid which separated was collected and crystallised from suitable solvents (Table 1).

4-Acetyl-2-aryl-4H-naphth[2,1-e]-1,3,4-oxadiazine-6-ol Acetate. General Procedure.- 2-Aroyl hydrazino-1,4-naphthoquinone (0.01 mol) was dissolved in acetic anhydride (15 ml) and treated with catalytic amounts of zinc powder and triethylamine. After refluxing on a steam bath for 6 hrs., the reaction mixture was cooled and poured over crushed ice and kept aside overnight. The solid which separated was collected and crystallized from suitable solvents (Table 1).

TABLE 2. Spectral Data of Compounds II, III and IV[a]

Cmp	R	^1H NMR (ppm)			IR (cm^{-1}) Nujol			
		NH	Ar-H	Other	NH	C=O (Quinone)	C=O (Amide)	Other
IIa	Ph	9.2 (b, 1H) 5.5 (b, 1H)	7.2-8.0 (m, 10H)	5.80 (s, 1H vinylic)	3330 3230	1640 -	1675 -	- -
IIIa	Ph	7.4-8.3 (m,10H)	-	2,3(s,3H, NAc)2.5(s, 3H,OAc)	-	-	1720	1690 (CO,OAc) 1200(COC) 1600(-N=C-)
IVa	Ph	-	-	-	3300	-	-	3370-3500 (b,-OH) 1610(-N=C-)

a)Mass spectrum of IIIa: m/e = 360 (M^+, 5), 298(10), 276(5), 256(11), 231(10), 105(100%). Mass spectrum of IVa: m/e = 276 (M^+, 15), 275(100%), 274(82), 273(98), 272(72), 157(15), 105(10), 90(20). NMR spectra of the compounds were recorded in $CDCl_3$.

2-Phenyl-4H-naphtho[2,1-e]-1,3,4-oxadiazine-6-ol. General Procedure.- 4-Acetyl-2-aryl-4H-naphtho[2,1-e]-1,3,4-oxadiazine-6-ol acetate (0.01 mol) was refluxed in 0.5% alcoholic sodium hydroxide solution on a steam bath for 30 min. The reaction mixture was cooled to 0° and neutralised with cold 1% HCl. The solid which separated was collected and crystallized from suitable solvents (Table 1).

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A CONVENIENT ONE-STEP SYNTHESIS OF AROYL CYANIDES FROM AROMATIC ALDEHYDES

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Acyl cyanides are versatile and important synthetic intermediates which have been utilized in a variety of transformations.[1] The acyl cyanides have been generally prepared by the reaction of acid halides with a variety of heavy metal (copper, silver or thallium) cyanides at high temperature.[2] Some modifications with cyanotrimethylsilane,[3] tributyltin cyanide,[4] potassium cyanide with ultrasound,[5] sodium cyanide with a phase-transfer catalyst,[6] or impregnated on Amberlite XAD resins[7] have been reported. Recently, oxidation of aromatic cyanohydrins to acyl cyanides catalyzed by $RuCl_2(PPh_3)_3$ has been described.[8] We now report a one-step method for the direct conversion of aromatic or heteroaromatic aldehydes 1 to the corresponding acyl cyanides 2.

$$\underset{\textbf{1a-d}}{RCHO} \xrightarrow[CrO_3]{KCN,TMSCl} \underset{\textbf{2a-d}}{RCOCN}$$

In method A (Eq. 1), the aromatic aldehyde 1 in dichloromethane was first allowed to react with two equiv. of potassium cyanide and one equiv. of trimethylsilyl chloride and stirred for 1 hr. Two equiv. of chromic anhydride was then added and the mixture was stirred until all the