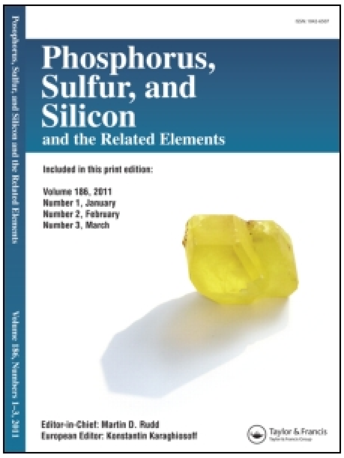

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF SOME NEW TYPES OF THIAZOLYL COUMARINS

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To cite this Article Rao, V. Rajeswar , Rao, G. Mohan , Kumar, V. Ravi and Vardhan, V. Aditya(1996) 'SYNTHESIS OF SOME NEW TYPES OF THIAZOLYL COUMARINS', Phosphorus, Sulfur, and Silicon and the Related Elements, 113: 1, 47 — 51

To link to this Article: DOI: 10.1080/10426509608046376

URL: http://dx.doi.org/10.1080/10426509608046376

Phosphorus, Sulfur, and Silicon, 1996, Vol. 113, pp. 47–51
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SYNTHESIS OF SOME NEW TYPES OF THIAZOLYL COUMARINS

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(Received September 3, 1995; in final form November 27, 1995)

3-Acetyl coumarins **I** react with substituted sulfanilamides in the presence of iodine to give substituted 3-(2-arylamino-4-thiazolyl)-2H-1-benzopyran-2-ones (**II**). The structures of these compounds have been confirmed and they were converted into their acetyl derivatives (**III**). Condensation of various 3-(ω-bromoacetyl)-2H-1-benzopyran-2-ones (**IV**) with rubenic acid in the presence of anhydrous ethanol and dimethyl formamide yielded 3,3'[2,2'-bithiazole]-4,4'-dylbis-[2H-1-benzopyran-2-one] (**V**). The structural assignment of these products is based on the elemental analyses and spectral (IR, PMR and MS) data.

Key words: (ω-bromoacetyl)coumarin, thiazole, N-acetyl thiazolyl coumarin.

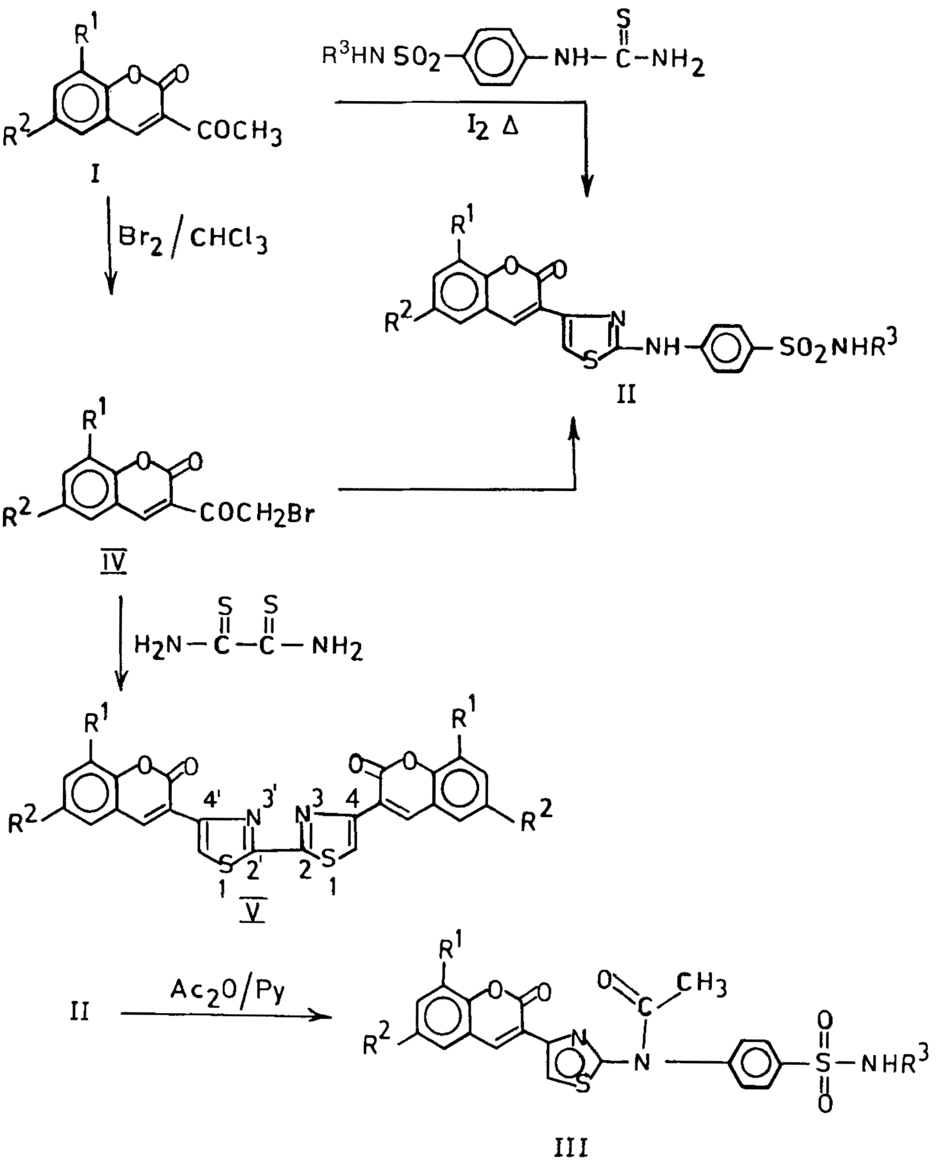
INTRODUCTION

Coumarins bearing one or more phenolic groups and containing a pyridyl moiety at the 3-position are spasmolytic and uricosuric agents.[1] Further thiazoles[2] and also coumarin derivatives with a heterocyclic system at the 3 position exhibit promising biological activities.[3] In view of this and in continuation of our earlier work on the synthesis of heterocyclic systems from coumarin derivatives[4–6] we report here the preparation of new heterocyclic thiazolyl coumarins starting from 3-acetyl coumarins.

RESULTS AND DISCUSSION

The substituted 3-thiazolyl coumarins have been prepared by two methods. According to the first method 3-acetyl coumarins are reacted with aryl thioureas in the presence of iodine to give **II**. The second method is a two step process in which the 3-acetyl coumarins are brominated with bromine[8] in chloroform to give **IV** which on reaction with aryl thioureas in anhydrous ethanol and DMF gave compounds of type **II**. Reaction of 3-(ω-bromoacetyl)coumarins with rubenic acid in a 2:1 molar ratio gave 3,3'[2,2'-bithiazole]-4',4'-diyl-bis[2H-1-benzopyran-2-one].

All the thiazolyl coumarins displayed strong absorption bands due to the thiazole[7] moiety at 1590, 1460, 1600 cm^{-1}. They also exhibited the typical lactone carbonyl frequency at 1720 cm^{-1}. The ^1H-NMR spectrum of **IIa** exhibited a characteristic singlet for the thiazole proton at δ 6.35. The remaining protons were observed in the expected regions. The structure of **IIa** to **IId** were further confirmed by preparing



their acetyl derivatives. The acetyl derivatives showed a strong IR absorption band at 1670 and 1690 cm^{-1} due to the amide and lactone carbonyl groups.

EXPERIMENTAL

All melting points were determined in open capillary tubes using a sulfuric acid bath and are uncorrected. IR spectra (ν_{max} cm^{-1}) were recorded on Perkin-Elmer 282 instrument. The ^{1}H-NMR spectra were recorded on a Varian 90 MHz spectrometer using tetramethylsilane as internal standard. Chemical shifts are expressed in δ ppm. Mass spectra were scanned on a Joel-JMS-300 spectrometer at 70 eV.

4-[[4-(2-oxo-2H-1-benzopyran-3-yl)-2-thiazolyl]amino]benzene sulphonamides (**IIA–IId**): A mixture of **I** (0.01 mol) iodine (0.02 mol) and sulfanilamide (0.01 mol) was heated on a water bath for 24 hr.

TABLE I

Analytical data of compounds **II**, **III**, **IV** and **V**

Compd	R^1 R^2	R^3 R^4	m.p.^{a} (°C)	Formule (m.w.)	Calcu. (Found %)	
					N	S
IIa	H H	H -	> 300	$C_{18}H_{13}N_3O_4S_2$ (399)	10.52 (10.48)	16.04 (15.98)
IIb	H Br	H -	200-202	$C_{18}H_{12}BrN_3O_4S_2$ (478)	8.78 (8.76)	13.39 (13.32)
IIc	Br Br	H -	220-222	$C_{18}H_{11}Br_2N_3O_4S_2$ (557)	7.54 (7.52)	11.49 (11.48)
IId	$-OCH_3$ -H	H -	240-242	$C_{19}H_{15}N_3O_5S_2$ (429)	9.79 (9.74)	14.92 (14.89)
IIIa	H H	H -	260-262	$C_{20}H_{15}N_3O_5S_2$ (441)	9.52 (9.50)	14.51 (14.48)
IIIb	Br H	H -	202-204	$C_{20}H_{14}BrN_3O_5S_2$ (520)	8.07 (8.00)	12.30 (12.26)
IIIc	Br Br	H -	217-219	$C_{20}H_{13}Br_2N_3O_5S_2$ (599)	7.01 (7.00)	10.68 (10.62)
Va	H H	- -	> 300	$C_{24}H_{12}N_2O_4S_2$ (456)	6.14 (6.12)	14.03 (13.98)
Vb	H Br	- -	> 300	$C_{24}H_{10}Br_2N_2O_4S_2$ (594)	5.23 (5.19)	11.96 (11.90)
Vc	Br Br	- -	223-225	$C_{24}H_{10}Br_2N_2O_4S_2$ (614)	4.56 (4.52)	10.42 (10.39)
Vd	$-OCH_3$ -H	- -	303-305	$C_{26}H_{16}N_2O_6S_2$ (516)	5.42 (5.40)	12.40 (12.37)

[a] All compounds were obtained in 70-80% yield. Satisfactory C, H analyses have been obtained. Compounds IIa to IId were crystallized from aq.DMF, IIIa-IIIc from ethanol, Va to Vd were from acetic acid.

The residue obtained was washed with ether, extracted with hot water and filtered. The filtrate on treatment with dilute ammonia liberated the free base which was filtered off, washed with water and crystallized viz., Table I.

Synthesis of **II** *from* **IV**: A mixture of **IV** (0.01 mol) and Sulphanilamide (0.01 mol) in anhydrous enthanol and dimethylformamide (each 6 ml) was refluxed for 3 hr when a solid separated out. The mixture was cooled and the solid filtered off, washed with water and crystallized from a suitable solvents viz., Table I.

Acetyl derivatives **II**: Compound **IIa–c** (0.01 mol) was dissolved in a minimum amount of acetic anhydride to which a drop of pyridine was added. The mixture was kept for 24 hr at room temperature. The obtained precipitate was filtered off, washed with cold water and crystallized viz., Table I.

3,3'-[2,2'-Bithiazole]-4,4'-diyl-bis[2H-1-benzopyran-2-one] **Va–d**: A mixture of **IV** (0.02 mol) and rubenic acid (0.01 mol) in anhydrous ethanol (6 ml) and dimethylformamide (6 ml) was refluxed for 4 hr when a solid separated out. The mixture was cooled, the solid filtered off, washed with water and crystallized viz., Table I.

Preparation of **Va–d** *from* **I**: A mixture of **I** (0.02 mol) and rubenic acid (0.01 mol) was heated with iodine (0.02 mol) on a water bath for 24 hr. The residue so obtained was washed with ether, extracted

TABLE II

Spectral data of compounds **II** to **V**

Compd	IR (ν_{max} cm^{-1})					^{1}H NMR (δ ppm)^a	Mass spectra (m/z %)
	-C=N	-NH-	NH_2	$-\overset{\overset{O}{\|}}{C}-O$ (lactone)	$-\overset{\overset{O}{\|}}{C}-NH$		
IIa	1570	3360	3460	1690	-	3.1 (s,1H NH), 6.85(s,1H,C_5H of thiazole) 7.0-7.6(m,8H,Ar-H), 8.35(s,1H,C_4H of coumarin), 10.25(s,2H,-SO_2 NH_2)	-
IIIa	1600	-	3460	1700	1675	3.3(s,3H,$-\overset{\overset{O}{\|}}{C}-CH_3$), 6.90(s,1H,$C_5$H of thiazole), 7.0-7.8(m,Ar-H), 8.40(s,1H C_4H of coumarin), 10.50(s,2H, -SO_2 NH_2)	-
Vd	1600	-	-	1720	-	4.0(s,6H,OCH_3), 6.80(s,2H,C_5-H of thiazole), 7.0-7.7(m,6H,Ar-H), 8.5(s, 2H, C_4H of coumarin)	Va 101(20%), 102(15%), 104(20%), 173(45%), 199(10%), 428(10%), 456(100%)

^{a}Compounds IIa, IIIa is in DMSO-d_6 and compound Vd in pyridine - d_5

with hot water and filtered. The filtrate on treatment with dilute ammonia liberated the free base which was filtered off, washed with water and crystallized. The compounds are identical with the compounds obtained form **IV** and rubenic acid (IR, mixed m.p. and TLC).

REFERENCES

1. W. Baker and C. S. Howese, *J. Chem. Soc.*, **119** (1953).
2. M. D. Friedmann, P. L. Stoller, T. H. Porter and K. Folkers, *J. Med. Chem.*, **16,** 1314 (1973).
3. S. N. Sawhney, S. P. Singh and S. K. Arora, *Indian J. Chem.*, **15B,** 727 (1977).
4. V. Rajeswar Rao, M. S. Rao and T. V. Padmanabha Rao, *Collect Czech Chem. Commun.*, **51,** 2214 (1986).
5. P. Ravinder, V. Rajeswar Rao and T. V. Padmanabha Rao, *Collect Czech Chem. Commun.*, **53,** 326 (1988).
6. S. Ramanna, V. Rajeswar Rao, T. Surya Kumari and T. V. Padmanabha Rao, *Phosphorous Sulfur and Silicon*, accepted for publication, July 22, 1995.
7. H. M. Raudell, R. N. Fusan, R. G. Fowler and J. R. Daugal, "IR Determination of Organic Molecules," Van Nostrand, New York 1949.
8. C. F. Koelsch, *J. Amer. Chem. Soc.*, **72,** 2993 (1950).