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Synthesis of Some 2-Phenyl Imino Thiazolidine Condensed Pyrimidines

A.K. SINGH*, B. KUMAR† and A.K. NAG
Department of Chemistry
Magadh University, Bodhgaya-824 234, India

2-Phenyl imino thiazolidin-4-one was prepared by well known method and treated with different aromatic aldehydes to yield corresponding benzylidine derivatives (1–3). These benzylidine derivatives when treated separately with urea and thiourea resulted in their corresponding thiazolidino pyrimidines (4–9) (Scheme II).

INTRODUCTION

Although the thiazolidinones are used as sedatives, analgesics etc. and pyrimidine nucleus occurs in a considerable number of natural products of vital importance to living organisms as uridine, cytidine, thymidine, deoxycytidine etc. and since a large number of thiazolidines[1] and pyrimidines[2] are known for their biological properties and also, due to the rare availability of thiazolidine and condensed pyrimidine ring componds, it was considered worth while to synthesise some new thiazolidino pyrimidines with substitution in both rings. Garnaik *et al.*[3] synthesised several compounds of thiazolidine condensed with other heterocyclic rings having biological activity. The spectral data of the compounds (Table 1) supports their structures.

TABLE-1

Compd. No.	IR Spectrum	UV Sectrum
4.	Absorption at 1575 cm^{-1} ν(C=N) 1280 cm^{-1} ν(C—S—C) 1465–1445 cm^{-1} ν(C—OH) 765 cm^{-1} (substituted benzene)	λ_{max} c.h.f 267, 290, 350 nm
5.	Absorption at 1590 cm^{-1} ν(C=N) 1480–1455 cm^{-1} ν(C—SH) 1270 cm^{-1} ν(C—S—C) 770 cm^{-1} (substituted benzene)	λ_{max} 265, 293, 365 nm
6.	Absorption at 1580 cm^{-1} ν(C=N) 1270 cm^{-1} ν(C—S—C) 1460–1440 cm^{-1} ν(C—OH) 750 cm^{-1} (substituted benzene)	λ_{max} c.h.f. 265, 294, 362 nm

† T.S. College Hisur

7.	Absorption at	1580 cm^{-1} ν(C=N) 1270 cm^{-1} ν(C—S—C) 1460–1440 cm^{-1} ν(C—S—H) 760 cm^{-1} (substituted benzene) 750 cm^{-1}(substituted benzene)	λ_{max} c.h.f. 263, 292, 340 nm
8.	Absorption at	1585 cm^{-1} ν(C=N) 1484–1450 cm^{-1} ν(C—S—H) 1260 cm^{-1} ν(C—S—C) 750 cm^{-1} (substituted benzene)	λ_{max} c.h.f. 264, 297, 362 nm
9.	Absorption at	1570 cm^{-1} ν(C=N) 1280 cm^{-1} ν(C—S—C) 1480–1450 cm^{-1} ν(C—S—C) 760 cm^{-1} (substituted benzene)	λ_{max} c.h.f. 267, 295, 360 nm

RESULTS AND DISCUSSIONS

The mechanism of thiazolidinone ring formation is very well known whereas for pyrimidine ring formation has great importance because it is not very clearly understood. However it is considered to proceed as follows.

Since benzylidinones were allowed to condense with urea and thiourea under suitable conditions, the benzylidine derivatives have α-β unsaturated cabonyl moiety which is expected to form the pyrimidine ring after condensation by way of attack on eletrophilic carbonyl carbon followed by elimination of water. The thiourea and urea undergo intramolecular rearrangment to yield pyrimidine.

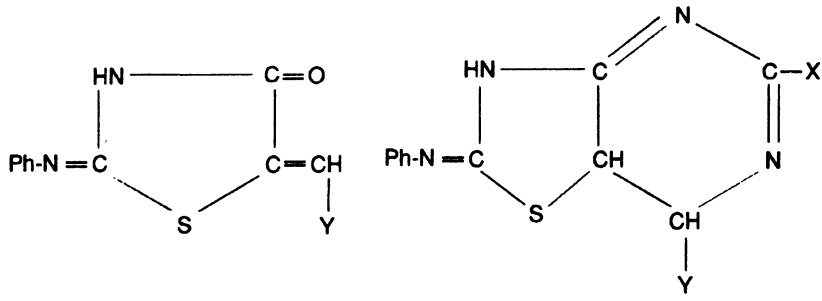
The other possible alternative arising by 1,4-addition of urea and thiourea results in the formation of pyrimidine (B). But in literature it is reported that pyrimidine (A) stucture is more suitable and more likely to be formed and most of the pyrimidines are formed by the reaction of unsaturated carbonyl compounds.

It is thus taken for granted that pyrimidine (B) is formed during the reaction. The adjoining thiazolidine ring is converted into thiazoline ring which can easily pass in to produce thiazole ring by possible tautomerisation. Thus the resulting compounds may be thiazole ring condensed pyrimidines. If pyrimidine (B) is formed then >C=N frequencies should disappear from the infrared spectra. But contarary to this expectation >C=N absorption peaks are distinctly observed in all the pyrimidines. Therefore pyrimidine (B) does not come in picture.

The structures of the substituted pyrimidine derivatives synthesised on the basis of pyrimidine (A). The structures have also been established on the basis of analytical and spectral studies. Thus the above synthesis opens a new knowledge in this particular field.

EXPERIMENTAL

The substituted thiazolidinone and its benzylidine derivatives were prepared by known methods and pyrimidines condensed with thiazolidine were synthesised as given. The melting points were determined in a Toshniwal melting point apparatus and are uncorrected. The purity of the compounds was monitored by TLC on silicagel G plates. These are soluble in hot acetic acid, sparingly soluble



(1-3) (4-9)

(1) Y = =>C_6H_6 (4, 6, 8)X = >OH

(2) Y = >P—$OCH_3C_6H_4$ (5, 7, 9)X = >SH

(3) Y = >3^1-$OCH_3$3^1-OHC_6H_3

(Scheme-I)

in ethanol and acetone and insoluble in non-polar solvents such as benzene, ether, etc. Physical and spectral data of the compounds are given in Table-1.

2-Phenyl imino thiazolidine Δ^2-2-hydroxy-6-phenyl (4,5-d) pyrimidine (4): 2-Phenyl imino 5-benzylidine thizaolidin-4-one (1 g), urea (1 g), glacial acetic acid (10 mL) and fused sodium acetate (0.5 g) were refluxed for 8 h on a water bath. After 1 h of refluxing all the contents were dissolved and after a few minutes light yellow crystals started appearing gradually. After cooling these were filtered, washed with alcohol and crystallised from glacial acetic acid. Yield obtained 2.1 g having m.p. = 298°C.

Found: C = 63.10, H = 4.34, N = 17.39% $C_{17}H_{14}N_4OS$ requires: C = 63.35, H = 4.34, N = 17.39%.

2-Phenyl imino thiazolidine Δ^2-2-thio-6-phenyl (4,5-d) pyrimidine (5): It was synthesised as compound (4) only by changing urea through thiourea. Yield obtained 2.3 g having m.p. = 300°C.

Formed C = 60.0, H = 3.85, N = 16.21%: $C_{17}H_{14}N_4S_2$ requires: C = 60.35, H = 4.14, N = 16.56%.

2-Phenyl imino thiazolidine Δ^2-2-hydroxy 6-p-methoxy phenyl (4,5-d) pyrimidine (6): 2-Phenyl imino 5-*p*-methoxy benzylidine thiazolidin-4-one (1 g) urea (1 g), glacial acetic acid (10 mL) and fused sodium acetate (0.5 g) were refluxed for 8 h on a water bath. After 1 h of refluxing all the contents were dissolved and after a few minutes deep yellow crystals started appearing gradually. The crystals were filtered, washed with alchohol and crystallised from glacial acetic acid. The yield obtained was 1.98 g having m.p. = 290°C.

Found: C = 61.00, H = 4.21, N = 15.61%. $C_{19}H_{16}N_4S_2O$ requires: C = 60.00, H = 4.20, N = 14.73%.

2-Phenyl imino thiazolidin Δ^2-2-thio 6-P-methoxy phenyl (4,5-d) pyrimidine (7): It was synthesised in the same manner as compound 6 only by changing urea by thiourea. Yield obtained was 1.95 g having m.p. = 282°C

Found: C = 59.73, H = 4.00, N = 14.42%. $C_{18}H_{16}N_4O_2S$ requires: C = 61.36, H = 4.54, N = 15.90%.

2-Phenyl imino thiazolidine Δ^2*-2-hydroxy 6(3'-methoxy 4'-hydroxy phenyl) (4,5-d) pyrimidine (8):* 2-Phenyl imino 5-(3'-methoxy 4'-hydroxy) benzylidine thiazolidin-4-one (1 g), urea (1 g), glacial acetic acid (10 mL) and fused sodium acetate (0.5 g) were refluxed for 8 h on a water bath. After 1 h of refluxing all the contents were dissolved and after a few minutes deep red crystals started appearing gradually. The crystals were filtered, washed with alchohol and crystallised from glacial acetic acid. yield obtained 2.2 g having m.p. = 275°C. Found: C = 58.3, H = 4.02, N = 15.00%. $C_{18}H_{16}N_4O_3S$ requires: C = 58.69, H = 4.34, N = 15.21%.

2-Phenyl imino thiazolidine Δ^2*-2-thio 6-(3'-methoxy 4'-hydroxy phenyl) (4,5-d) pyrimidine (9):* It was synthesised as compound 8 only by changing urea by thiourea. Yield obtained 2.1 g having m.p. = 272°C.

Found: C = 57.25, H = 3.75, N = 13.85%. $C_{19}H_{16}N_4S_2O_2$ requires: C = 57.57, H = 4.04, N = 14.14%.

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REFERENCES

1. R.R. Shah, R.D. Mehta and A.R. Parikh, *J. Indian Chem. Soc.*, **62**, 255 (1985).
2. A.K. Sengupta and Ashok K. Panday, *J. Indian Chem. Soc.*, **65**, 142 (1988).
3. Bama K. Garnaik and Rajani K. Behra, *J. Indian Chem. Soc.*, **65**, 456 (1988).
4. Lina Mehta and Hansa Parekh, *J. Indian Chem. Soc.*, **65**, 65 (1988).
5. C.L. Patel and Hansa Parekh, *J. Indian Chem. Soc.*, **65**, 282 (1988).
6. (Miss) Maitreyee Debi, *J. Indian Chem. Soc.*, **66**, 418 (1989).
7. Abdul U. Siddiqui and A.H. Siddiqui, *J. Indian Chem. Soc.*, **71**, 107 (1994).
8. Gamal A. Ahmad, *J. Indian Chem. Soc.*, **72**, 181 (max) (1995).
9. S.S. Mandal, P.C. Ghorai, S. Rai and H.K. Saha, *J. Indian Chem. Soc.*, **72**, 807 (1995).

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