

NOTE

Synthesis of Some N-Amino Quinolin-2-ones from 4-Methyl Coumarins

A.D. GHARDE

Department of Chemistry, Nutan Adarsha College
Umrer, Distt. Nagpur-441 203, India

4-Methyl coumarins readily react with hydrazine hydrate in alkaline medium to give N-amino-quinolin-2-ones. The compounds were characterised by elemental analysis, chemical properties and IR and NMR spectra.

In an earlier communication¹ synthesis of 4-styryl coumarins was reported. Review² of the synthesis of coumarins by Pechmann condensation of resorcinol, *m*-cresol and *p*-cresol with ethyl acetoacetate in presence of different condensing agents (*i.e.*, iodine, bromine, sulphuric acid, PCl_3 , P_2O_5 and AlCl_3) is well known. Replacement of heterocyclic oxygen atom in some other series is known³⁻⁵. The present work deals with the synthesis of new quinolin-2-one derivatives from coumarins, by replacing -O atom by -N atom.

Coumarins (1 and 2) with hydrazine hydrate in alkaline medium gave quinolin-2-ones (5 and 6); acetylation of 5 and 6 gave the corresponding N-acetyl derivatives 7 and 8 respectively. The new compounds were identified by elemental analysis, chemical properties and spectral data.

7-Hydroxy or 7-hydroxy-6-chloro-4-methyl coumarin (3 and 4) was recovered unchanged when allowed to react with hydrazine hydrate. Thus the reaction is possible in presence of methyl substituent in phenyl ring to give quinolinones. It was reported that in the formation of dicoumarol⁶ it is necessary to have the hydroxyl group in phenyl ring. A numbers of reactants were used, *viz.*, $\text{NH}_2\text{OH}\cdot\text{H}_2\text{O}$; $\text{NH}_2\text{OH}\cdot\text{HCl}$; PhNHNH_2 and ArNH_2 . Hydrazine hydrate was found to give the desired product rapidly. The new quinolinones prepared during this work are given in Table-2 and previously known coumarins but synthesized for the study of the reaction are given in Table-1.

Preparation of Coumarins (1 to 4)

The respective phenol (0.1 mol) and ethylacetoacetate (0.1 mol) were dissolved in sulphuric acid (75%, 20 mL). The mixture was stirred well and kept overnight. It was then diluted with ice-cold water; the solid obtained was crystallized from

For correspondence: Dr. A.D. Gharde, C/o. S.C. Banait, Rahate Layout, Parsodi, UMRER, Disit: NAGPUR-441 203, India

rectified spirit to get coumarins (1 to 4). The m.p., yield and references are given in Table-1.

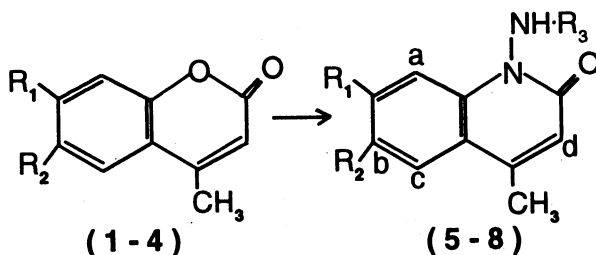


TABLE-1
PHYSICAL DATA OF COUMARINS

Coumarin	—R ₁	—R ₂	Yield (%)	m.p. °C (Lit.)/ m.p. °C (Ref.)
1.	CH ₃	H	70	134/134 ²
2.	H	CH ₃	50	148/148 ²
3.	OH	H	90	184/185 ²
4.	OH	Cl	80	280/280 ⁷

Preparation of N-amino quinolin-2-ones (5 and 6)

Coumarin (1 and 2) (0.01 mol) and anhydrous potassium carbonate (5 g) were taken in ethanol (30 mL). Hydrazine hydrate (0.01 mol) was added dropwise while the reaction mixture was refluxed for 5 h. It was cooled and excess of ethanol was distilled off. The solid separated was washed with water, dried and then washed with benzene. 5 and 6 are white crystalline solids. m.p. and yields are given in Table-2

TABLE-2
QUINOLIN-2-ONES AND ACETYL DERIVATIVES

Quinolinone	—R ₁	—R ₂	—R ₃	Yield (%)	m.p. (°C)
5.	CH ₃	H	H	50	190
6.	H	CH ₃	H	45	202
7.	CH ₃	H	COCH ₃	70	120
8.	H	CH ₃	COCH ₃	60	139

Spectra of 5: IR (ν_{\max}): 3400–3100 ν (broad, H bonding N—NH₂), 1705 ν (CO), 1570 (phenyl ring), 1380 ν (C—CH₃) and 1240 ν (C—N); 1120, 1065, 875, 810 cm^{-1} other characteristic peaks.

¹H NMR: δ 2.38, s, 6H (2 × C—CH₃); 6.02, s, 1H (Hd); 6.85, d, 2H (Hb, Hc); 7.35, s, 1H (Ha); 9.4 broad, 2H (—NH₂) (—NH—H—OC).

Acetylation of N-amino quinolin-2-ones (5 and 6)

A mixture of 5 or 6 (0.01 mol), acetic anhydride (0.01 mol) and fused sodium acetate (0.5 g) was heated on water bath for 40 min. The reaction mixture was

diluted with cold water and the solid separated was filtered and crystallized from rectified spirit to obtain 7 and 8.

ACKNOWLEDGEMENTS

Thanks are due to RSIC, Lucknow and RSIC, I.I.T., Powai, Mumbai for elemental analysis and spectral data and also to U.G.C., New Delhi for giving financial assistance under minor research project. Thanks are also due to Dr. B.J. Ghiya for his keen interest and guidance during the course of this work.

REFERENCES

1. A.D. Gharde and B.J. Ghiya, *J. Indian Chem. Soc.*, **69**, 397 (1991).
2. S. Sethna and R. Phadke, *Org. React.*, **7**, 7 (1953).
3. U.C. Meshelkar, P.A. Thakur and K.V. Walavalkar, *Indian J. Het. Chem.*, **1**, 201 (1991).
4. H.M. Patel and K.R. Desai, *Indian J. Het. Chem.*, **1**, 43 (1991).
5. G. Achaiah, Y. Jayamma and V.M. Reddy, *Indian J. Het. Chem.*, **1**, 39 (1991).
6. A.D. Gharde and B.J. Ghiya, *J. Indian Chem. Soc.*, **72**, 209 (1995).
7. D. Chakravarti and B. Ghosh, *J. Indian Chem. Soc.*, **12**, 622 (1935).

(Received: 11 October 1999; Accepted: 14 December 1999)

AJC-1961