Asian Journal of Chemistry Vol. 14, No. 2 (2002), 1053–1055

NOTE

Synthesis of 2-(Substituted Benzylidene)-7-Substituted-5-Chloro Coumaran-3-One

S.V. KOLHE*, A.G. DOSHI and A.W. RAUT
Postgraduate Department of Chemistry Shri Shivaji Science College, Morshi Road, Amravati-444 603, India

2-Hydroxy substituted chalcone (**Ia–p**) was dissolved in DMSO and mercuric acetate was added to it. The reaction mixture was refluxed for 2–3 h and then diluted with water. The solid separated was crystallised from rectified spirit to give coumaran-3-ones (**IIa–p**) (Aurones). The structural elucidation of compound were done on the basis of analytical and spectral data.

Key words: Synthesis, 2-Substituted benzylidene)-7-substituted-5-chloro coumaran-3-one.

Presence of 6′-position in chalcone gives aurones in AFO reaction instead of flavanol[1]. Chalcone dibromide on alkali treatment gives flavone[2]. However if chalcone dibromide is kept in cold ethanol for 24 h then treated with alkali, only aurones are obtained[3, 4]. We come across on interesting reaction of mercuric acetate in DMSO on chalcone. The cyclisation of chalcones have been reported by earlier workers[5]. Mercuric acetate has been used in various synthesis specially in dehydrogenation of ergosterol and vitamin D, acetoxylation of olefins and ketones, oxidation of tertiary amine to enamines, as catalyst in vinyl ester interchange and bromination, formation of mercurated aromatic compounds and acetylation[6]. While DMSO as a well known solvent for elimination reaction[7, 8]. Flavones react with bromine in acetic acid in presence of mercuric acetate as a catalyst to give 3-bromo flavones[9]. 2′-Hydroxy chalcones in acetic acid reacts with $Mn(OAc)_2$ gave aurones[10]. Mercuric acetate-DMSO has been used for the synthesis of aurones[11–13].

Hence it was interesting to prepare aurones from new chalcones. Aurones have been studied for their utilization in the synthesis of different heterocyclic compounds by O'Sullivan[14]. Chalcones were prepared by known method[15].

Melting points were determined in an open capillary tube and are uncorrected. IR spectra were recorded on Perkin-Elmer 557 spectrophotometer. PMR spectra were recorded in $CDCl_3$ on a Bruker AC 300F spectrophotometer at 300 MHz

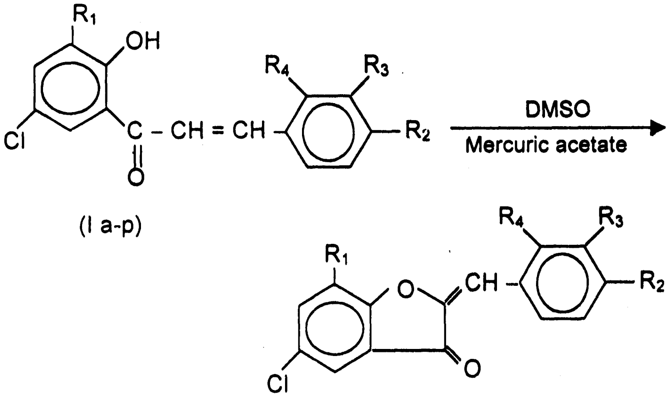
---

*Address for correspondance: S.V. Kolhe, c/o. Dr. A.W. Raut, 23, Keshav Colony, Camp, Amaravati-444 603 (India).

were recorded in $CDCl_3$ on a Bruker AC 300F spectrophotometer at 300 MHz using TMS as an internal reference. Purity of the compounds was checked on silica gel-G coated plates.

Synthesis of 2-(Substituted Benzylidene)-7-Substituted-5-Chloro Coumaran-3-one

2-Hydroxy-3-nitro-5-chloro-4′-methoxy chalcone **(Ia)** (0.01 mole) was dissolved in 20 mL DMSO and mercuric acetate (0.01 mole) was added. The mixture was refluxed for 2 to 3 h, cool, diluted with ice cold water, washed with water several time. The resulting solid was crystallised from ethanol to get aurone **(IIa)**. The structure of compound have been supported by spectral and chemical data.



(I a-p)

(II a—p)

Properties of the compound (IIa)

It is a faint yellowish crystalline solid, m.p. 150°C, showing negative ferric chloride test, indicating involvement of phenolic hydroxy group in cyclisation. m.f. $C_{16}H_{10}NO_5Cl$, m.w. = 331.6, elemental analysis (%), found (calcd.): C = 48.25 (48.29), H = 3.01 (3.02), N = 4.21 (4.20).

The IR spectrum was recorded on Perkin-Elmer 557 Spectrophotometer. 1704. (C=O stretching in cyclic ketone); 1647 (C=C stretching); 1589 and 1341 (symmetrical aromatic —NO_2); 1262 (stretching aromatic ring); 1205 (C—O—C stretching in 5-membered cyclic ketone); 1030 (—OCH_3 stretching in aromatic ether); 766 cm^{-1} (C—Cl stretching).

The PMR was recorded in $CDCl_3$ with TMS as an internal standard. 3.88 δ (s, 3H, aromatic —OCH_3); 6.9–7.6 δ (m, 6H, aromatic —H); 7.8 δ (s, 1 H, =CH).

These chemical, spectral data shows that compound **(IIa)** is 2-(4′-methoxy benzylidene)-7-nitro-5-chloro-coumaran-3-one.

Similarly other compounds were prepared by above method and reported in Table-1.

TABLE-1
SYNTHESIS m.p. AND YIELD (%) OF SUBSTITUTED COUMARAN-3-ONE

Comp. No.	R_1	R_2	R_3	R_4	m.p. (°C)	Yield (%)
IIa	NO_2	OCH_3	H	H	150	62
IIb	NO_2	H	H	H	152	66
IIc	NO_2	H	H	OH	86	69
IId	NO_2	H	NO_2	H	174	70
IIe	H	H	H	H	154	59
IIf	H	OCH_3	H	H	155	68
IIg	H	H	H	OH	163	67
IIh	H	H	NO_2	H	165	78
IIi	Br	H	H	H	114	74
IIj	Br	OCH_3	H	H	183	79
IIk	Br	H	H	OH	208	60
IIl	Br	H	NO_2	H	172	65
IIm	Cl	H	H	H	118	80
IIn	Cl	OCH_3	H	H	155	66
IIo	Cl	H	H	OH	90	62
IIp	Cl	H	NO_2	H	163	70

REFERENCES

1. J. Algar and J.P. Flynn, *Proc. Irish Acad.*, **42B**, 1,(1934).
2. T.A. Geirsman and D.K. Funkushma, *J. Am. Chem. Soc.*, **70**, 1986 (1948).
3. T.S. Wheeler, *Proc. Ind. Acad. Sci.*, **2**, 39 (1935), *J. Chem. Soc.*, 1978 (1937).
4. M.G. Marathey, *J. Uni. Poona*, **2**, 7 (1952).
5. Christorophey O'Miles and Lyndsay Mash, *Perkin Trans.*, **11**, 1623 (1989).
6. Fisher and Fisher, Reagents from Organic Synthesis, pp. 296-309, 644–651 (1967).
7. A.G. Doshi, P.A. Soni, and B.J. Ghiya, *Indian J. Chem.*, **25B**, 759 (1986).
8. P.D. Lokhade and B.J. Ghiya, J. *Indian Chem. Soc.*, **68**, 412 (1991).
9. S.S. Sonare and A.G. Doshi, *J. Indian Chem. Soc.*, **69**, 879 (1992).
10. Kurosawa Kazu, *Bull, Chem. Soc. (Japan)*, **42**, 1456 (1969).
11. A.S. Sahastrabuddhe, Ph.D. Thesis, Nagpur Uni. (1992).
12. S.K. Doifode and A.G. Doshi, *Oriental J. Chem.*, **11**, 189 (1995).
13. V.B. Kadu and A.G. Doshi, *Oriental J. Chem.*, **13**, 281 (1997).
14. W, Lov O'sullivan *J. Chem. Soc. Perkin Trans.*, **1**, 115 (1981); 1557 (1989).
15. A.G. Doshi and B.J. Ghiya, *Curr. Sci. (India)*, **55**, 502 (1989).

(*Received:* 16 September 2001; *Accepted*: 15 February 2002) AJC-2633