

NOTE

Synthesis and Properties of Some 3-Halo Flavones

R.E. BHADANGE, A.G. DOSHI and A.W. RAUT*

*Postgraduate Department of Chemistry**Shri Shivaji Science College, Morshi Road, Amravati-444 602, India*

2-Hydroxy-3-substituted-5-chloro-4'-nitro dibenzoyl methane, 2-hydroxy-3-substituted-5-chloro-4'-amino dibenzoyl methane and 2-hydroxy-3-substituted-5-chloro-4'-chloro dibenzoyl methane react with iodine monochloride in DMF medium or with bromine in DMF medium affording respectively 2-(4'-substituted) 3-halo-6-chloro-8-substituted flavone. The structure of these compounds is confirmed by chemical and spectral data.

Key words: Synthesis, properties, 3-halo flavones.

Propane-1,3-dione reacts with dioxane dibromide to give 3-bromo flavone¹. β -Dicarbonyl compounds have been effectively chlorinated using sulphuryl chloride to form 3-chloro flavones. Acetyl acetone has been chlorinated with sulphuryl chloride in acetic acid².

Dibenzoylmethane gives α -chlorodibenzoyl methane with sulphuryl chloride in dioxane³. 3-Chloroflavones were prepared by the action of thionylchloride or sulphuryl chloride with flavone⁴⁻⁶.

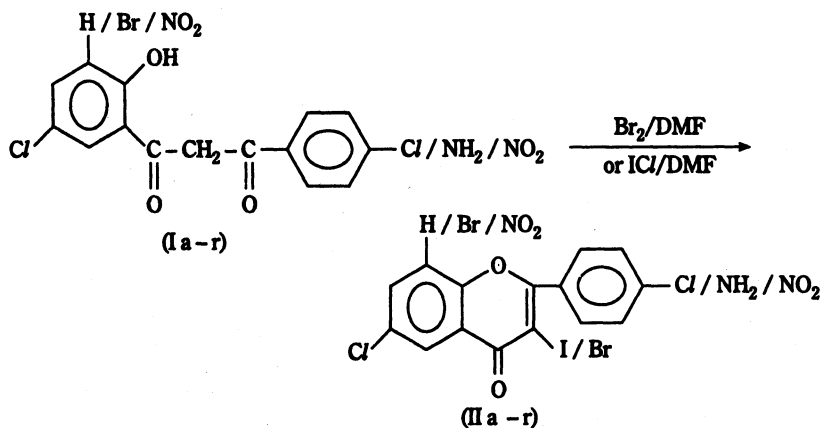
Recently Thakare prepared 3-chloro/3-bromo/3-iodo-2-furyl chromones when 1-(2'-furyl)-3-(2''-hydroxy-3''-substituted-5''-chlorophenyl)-1,3-propane diones react with corresponding sulphuryl chloride in dioxane, bromine in dioxane and iodine monochloride in dioxane⁷.

Literature survey indicates that 3-halo flavone are not prepared from 2-hydroxy-3-substituted-5-chloro-4'-substituted dibenzoyl methane. Hence we thought to synthesise them. The diketones were prepared by known method⁸.

General procedure for preparation of 3-halo flavone

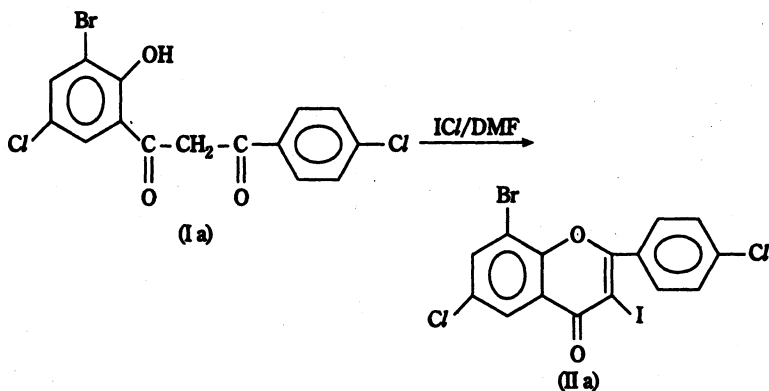
2-Hydroxy-3-substituted-5-chloro-4'-substituted dibenzoyl methane (**Ia-r**) was dissolved in dimethyl formamide and pure iodine monochloride or bromine in dioxane was added. The mixture was refluxed for 1.30 h, cooled, diluted with ice-cold water and a solid was obtained. It was crystallised from ethanolic acetic acid mixture to get 2-(4'-substituted) 3-halo-6-chloro-8-substituted flavone (**IIa-r**).

*Address for correspondence: Dr. A.W. Raut, 23, Keshav Colony, Camp, Amravati-444 602, India.



Preparation of 2-(4'-chlorophenyl)-3-iodo-6-chloro-8-bromo flavone

2-Hydroxy-3-bromo-5-chloro-4'-chloro dibenzoyl methane (**Ia**) (0.01 mole) was dissolved in dimethyl formamide (DMF) and pure iodine monochloride (0.01 mole) was added. The mixture was refluxed for 1.30 h, then cooled, diluted with ice-cold water and crystallised from alcohol-acetic acid mixture to get 2-(4'-chlorophenyl)-3-iodo-6-chloro-8-bromo flavone (**IIa**), m.p. 205°C, yield 80%.



Properties of compound **IIa**

It is leaf-brown crystalline compound having m.p. 205°C. It shows negative ferric chloride test indicating involvement of phenolic hydroxy group in cyclization. The IR spectrum recorded in nujol shows the following bands: 1663 $\nu(\text{C}=\text{O})$, 1595, 1555, 1459 ($\text{C}=\text{C}$ in aromatic ring), 1284 (Ar—O), 763 ($\text{C}-\text{Cl}$), 702 ($\text{C}-\text{Br}$) and 546 cm^{-1} ($\text{C}-\text{I}$).

The PMR was recorded in CDCl_3 with TMS as internal standard. 6.80–8.20 δ (m, 6H, Ar—H).

The other 3 halo flavones are prepared by general procedure as listed in Table-1

TABLE-1
SYNTHESISED 3-HALO FLAVONES, m.p., YIELD, COLOUR AND m.f.

S.No.	R ₁	R ₂	R ₃	m.p. (°C)	Yield (%)	Colour	m.f.
IIa	Br	Cl	I	205	80	Leaf brown	C ₁₅ H ₆ O ₂ BrCl ₂ l
IIb	Br	Cl	Br	179	75	Mid buff	C ₁₅ H ₆ O ₂ BrCl ₂
IIc	Br	NO ₂	I	169	60	Brown	C ₁₅ H ₆ NO ₄ BrClI
IId	Br	NO ₂	Br	109	79	Mercedes red	C ₁₅ H ₆ NBr ₂ Cl
IIe	Br	NH ₂	I	174	76	Imp crimson	C ₁₅ H ₈ NO ₂ BrClI
IIf	Br	NH ₂	Br	136	65	Dark brown	C ₁₅ H ₈ NO ₂ Br ₂ Cl
IIg	NO ₂	Cl	I	132	69	Suede	C ₁₅ H ₆ NO ₄ Cl ₂ l
IIh	NO ₂	Cl	Br	204	72	Mid buff	C ₁₅ H ₆ NO ₄ BrCl ₂
IIi	NO ₂	NO ₂	I	250	75	Mid buff	C ₁₅ H ₆ N ₂ O ₆ ClI
IIj	NO ₂	NO ₂	Br	195	78	Brown	C ₁₅ H ₆ N ₂ O ₆ BrCl
IIk	NO ₂	NH ₂	I	144	73	Dark brown	C ₁₅ H ₈ N ₂ O ₄ ClI
III	NO ₂	NH ₂	Br	130	75	Leaf brown	C ₁₅ H ₈ N ₂ O ₄ BrCl
IIm	H	Cl	I	239	79	Mushroom	C ₁₅ H ₇ O ₂ Cl ₂ l
II n	H	Cl	Br	224	80	Mid buff	C ₁₅ H ₇ O ₂ BrCl ₂
IIo	H	NO ₂	I	295	76	Tata mimosa	C ₁₅ H ₇ NO ₄ BrClI
IIp	H	NO ₂	Br	298	79	Mid buff	C ₁₅ H ₇ NO ₄ BrCl
IIq	H	NH ₂	I	320	77	Golden brown	C ₁₅ H ₉ NO ₂ ClI
IIr	H	NH ₂	Br	262	75	Leaf brown	C ₁₅ H ₉ NO ₂ BrCl

REFERENCES

1. K.N. Wadodkar and K.B. Doifode, *Indian J. Chem.*, **18B**, 458 (1979).
2. J.P. Park, Brown and J.D. Lachar, *J. Am. Chem. Soc.*, **75**, 4753 (1953).
3. H.L. Gaggad and K.N. Wadodkar, *Indian J. Chem.*, **17B**, 141 (1979).
4. J.R. Merchant and D.V. Rege, *Chem. Commun.*, 380 (1970).
5. F. Camer and G. Elshmg, *Ber dt. Chem. Ges.*, **89**, 1 (1956).
6. J.R. Merchant, D.V. Rege and A.R. Bhat, *Indian J. Chem.*, **10**, 142 (1972).
7. S.S. Thakare, Ph.D. Thesis, Amravati University (2001).
8. R.E. Bhadañge, A.G. Doshi and A.W. Raut, *Asian J. Chem.*, **13**, 1152 (2001).

(Received: 16 August 2001; Accepted: 23 November 2001)

AJC-2534