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A Facile Transformation of E-3-Benzylideneflavanones to 3-(α-Hydroxybenzyl)flavones

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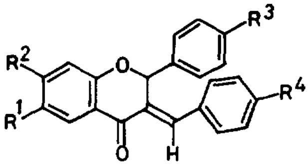
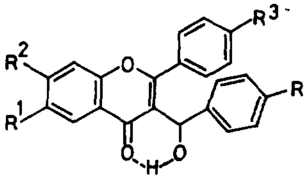
Abstract: During reaction of E-3-benzylideneflavanones with NBS/dibenzoyl peroxide in CCl_4 3-(α-hydroxybenzyl)flavones are formed, possibly through involvement of moisture. Copyright © 1996 Published by Elsevier Science Ltd

In 1988 Dhande *et al.*[1] reported that E-3-benzylideneflavanones (**1**) could be photochemically oxidised (O_2, CHI_3, hν) to 3-(α-hydroxybenzyl)flavones (**2**) but this conversion could not be effected through bromohydrin formation (with NBS/aq. acetone) followed by HBr elimination. As an extension of our recent studies on **1**[2] we planned first to brominate them with NBS/CCl_4, then to hydrolyse the bromo derivative to form **2**. An interesting observation obtained in this study is presented herein.



1



2

a: $R^1=R^2=R^3=R^4=H$; **b:** $R^1=R^2=R^3=H,R^4=Cl$; **c:** $R^1=R^2=H,R^3=R^4=Cl$;
d: $R^1=R^2=H,R^3=OMe,R^4=Cl$; **e:** $R^1=H,R^2=OMe,R^3=R^4=Cl$; **f:** $R^1=R^2=R^3=H,R^4=NO_2$;
g: $R^1=Me,R^2=R^3=R^4=H$; **h:** $R^1=CH_2Br,R^2=R^3=R^4=H$.

We first carried out the reaction of **1a** (NBS, dibenzoyl peroxide)[3,4] in $CaCl_2$-dried CCl_4 under reflux condition. Within 8 hr. the starting material disappeared completely yielding a product, which, to our pleasant surprise, was 3-(α-hydroxybenzyl)flavone (**2a**). Extending the study to **1b-f** the same result was obtained (Table). Reaction at room temperature was much slower (almost complete after 5 days), but that also yielded the same product.

Table

E-3-Benzylidene-flavanone	Product	Yield (%)	M.P. (°C)	Characteristic ^{1}H NMR signals (δ)$^+$	
				>CH-	-OH
1a	**2a**	77	173-74	5.72(d)	5.26(d)
1b	**2b**†	71	149-50	5.70(br.s)	5.24(br.peak)
1c	**2c**	63	122-23	5.66(d)	5.24(d)
1d	**2d**	67	liq.	5.66(d)	5.14(d)
1e	**2e**	65	180-81	5.64(d)	5.28(d)
1f	**2f**	66	164-65	5.81(d)	5.17(d)

$^+$The signals underwent expected change on D_2O shaking.

$^†M^{+\cdot}$ 362, 364

The mechanism of conversion of 1 to 2 under these reaction conditions could not be fully understood. That it is not an example of benzoyl peroxide initiated autoxidation was evident from the recovery of the starting material by conducting the reaction in absence of NBS, but otherwise under identical conditions. A possibility, therefore, is the involvement of trace amount of moisture (either present in solvent and reagents or entered through the $CaCl_2$ guard tube used), which either causes rapid hydrolysis of an intermediate bromo compound or directly takes part during NBS reaction. However, the results of the following experiments clearly show that other bromination reactions do not change their usual course :

1a (1 mol.) + *p*-Nitrotoluene (1 mol.) $\xrightarrow{a}$ **2a** + *p*-Nitrobenzyl bromide

1a (1 mol.) + Fluorene (1 mol.) $\xrightarrow{a}$ **2a** + 9-Bromofluorene

2g + **2h** (1:3) $\xleftarrow{a}$ **1g** $\xrightarrow{b}$ **2g** + **2h** (10:1)

a: NBS (2 mol.), dibenzoyl peroxide, CCl_4, reflux, 10 hr.

b: NBS (1 mol.), dibenzoyl peroxide, CCl_4, reflux, 10 hr.

The unusual reactivity of E-3-benzylideneflavanone system is therefore noteworthy.

Thus, we have developed a simple method for conversion of E-3-benzylideneflavanones **(1)** to 3-(α-hydroxybenzyl)flavones **(2)**. The method may find application for effecting a similar conversion in analogous systems.

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References and Notes

1. Dhande,V.P.; Thakwani,P.; Marathe,K.G.; *Tetrahedron*, 1988, **44**, 3015.
2. (a) Mallik,U.K.; Saha,M.M.; Mallik,A.K.; *J.Indian Chem.Soc.*, 1990, **67**, 478.
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   (c) Dhara,M.G.; Mallik,U.K.; Mallik,A.K.; *Indian J.Chem.*, 1996, **35B**, 0000.
3. NBS was crystallised from glacial acetic acid and dried in vacuum over KOH beads and fused $CaCl_2$; m.p. 182°.
4. Substrate (1 mmol) + NBS (1 mmol) + Dibenzoyl peroxide (2 mg).

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