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Novel conversion of 3-(α-hydroxybenzyl)flavones to 3-benzoylchromones and 3-cyanoflavones with NaN_3/TFA

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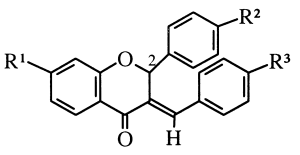
Abstract

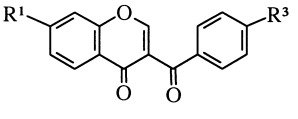
On treatment with NaN_3/TFA, 3-(α-hydroxybenzyl)flavones are converted to 3-benzoylchromones and 3-cyanoflavones, plausible mechanisms for which have been suggested.

Keywords: 3-(α-hydroxybenzyl)flavones; sodium azide/TFA; 3-benzoylchromones; 3-cyanoflavones.

On extending our current studies on reactions of *E*-3-benzylideneflavanones (**1**)[1] to the Schmidt reaction some novel observations were obtained. Thus, on treatment with NaN_3/TFA in air several compounds yielded 3-benzoylchromones (**2**) by loss of the 2-aryl group as the corresponding aniline.[1d] An aerial oxidation of intermediate 3-(α-hydroxybenzyl)chromones or corresponding trifluoroacetates has been suggested to explain the occurrence of such products. 3-(α-Hydroxybenzyl)flavones (**3**) are readily obtainable from **1** by reaction with NBS,[1a] and as **3** could be considered as oxidation products of **1** we became interested in studying the reaction of the former with NaN_3/TFA. The novel aspects of this reaction are presented in this communication.



1



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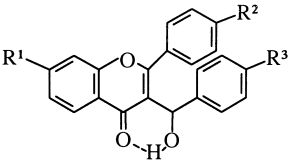

3

When the unsubstituted 3-(α-hydroxybenzyl)flavone **3a** was treated with 1 equivalent of NaN_3 in TFA (rt, four days) it underwent ca. 80% conversion yielding 3-benzoylchromone (**4a**) as the only product in moderate yield. Complete conversion of the substrate under the same reaction

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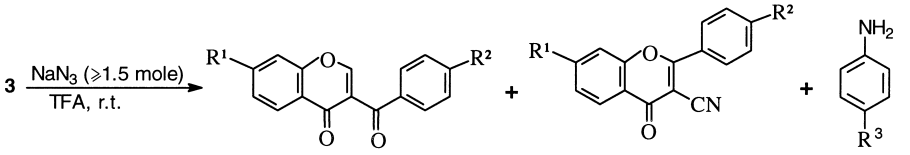
conditions was observed by use of 1.5 equivalents of NaN_3. However, in this case another product, characterised as 3-cyanoflavone (**5a**), was obtained in poor yield. The second product could be obtained as the major product by use of still greater proportions of NaN_3. Similar results were obtained from other 3-(α-hydroxybenzyl)flavones **3b–f** (Table 1). On making the aqueous solution left after ether extraction of the diluted reaction mixture alkaline, an aniline corresponding to the phenyl group of the α-hydroxybenzyl moiety was obtained in each case.

Table 1



4 **5**

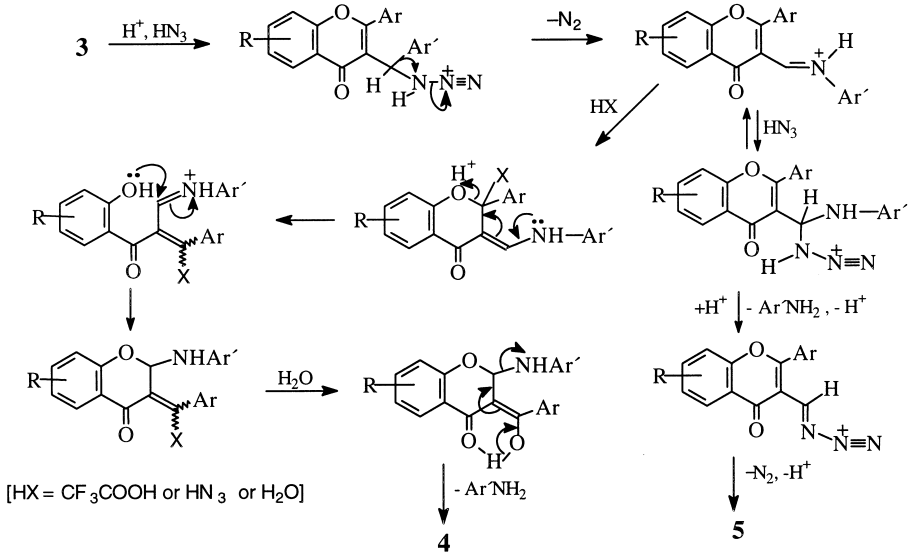
a: $R^1=R^2=H$; **b**: $R^1=H$, $R^2=OMe$;

c: $R^1=H$, $R^2=Cl$; **d**: $R^1=OMe$, $R^2=H$;

Substrate (**3**) (1 mmole)	Amount of NaN_3 (mmole)	Products[2] (Yield, %)	
3a	1.5	**4a** (36)	**5a** (5)
($R^1=R^2=R^3=H$)	2.5	**4a** (10)	**5a** (28)
3b	1.5	**4a** (52)	**5a** (16)
($R^1=R^2=H$, $R^3=OMe$)	2.5	**4a** (26)	**5a** (32)
3c	1.5	**4a** (25)	**5a** (7)
($R^1=R^2=H$, $R^3=Cl$)	2.5	**4a** (10)	**5a** (24)
3d	1.5	**4b** (34)	**5b** (5)
($R^1=H$, $R^2=OMe$, $R^3=Cl$)	2.5	**4b** (12)	**5b** (26)
3e	1.5	**4c** (28)	**5c** (7)
($R^1=H$, $R^2=R^3=Cl$)	2.5	**4c** (8)	**5c** (31)
3f	1.5	**4d** (36)	**5d** (16)
($R^1=OMe$, $R^2=R^3=H$)	2.5	**4d** (18)	**5d** (29)

The mechanisms delineated in Scheme 1 may be suggested for the formation of **4** and **5** from **3**. In order to account for the results, migration of the phenyl group of the α-hydroxylbenzyl moiety to an electron deficient nitrogen becomes necessary in all the examples. This prompted us to study the reaction of **3g** (**3** with $R^1=R^2=H$, $R^3=NO_2$) and in this case no product of the series **4** and **5** was obtained.[3]

Thus, we report a novel result originating from a simple reaction of 3-(α-hydroxybenzyl)-flavones (**3**). Although the benzopyrone moiety present in **3** is responsible for the formation of **4**, the transformation **3**→**5** appears to be a reaction typical of secondary alcohols. To our knowledge, among a number of existing reports of reactions of secondary alcohols with HN_3,[4] none mentions splitting of such compounds into amines and cyanides. The present study therefore has potential to be extended to many other structurally related substrates.



Scheme 1.

Acknowledgements

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References

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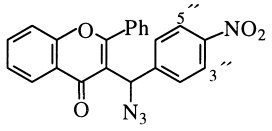
2. The 3-benzoylchromones **4a**–**d** are known compounds.[1d] Selected data of **5**: **5a** mp 151–152°C. Anal.: found C, 77.41; H, 3.81; N, 5.40%; calcd for $C_{16}H_9NO_2$ C, 77.72; H, 3.67; N, 5.66%. IR (ν, KBr, cm^{-1}): 2210 (C≡N), 1645 (C=O). ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (1H, dt, $J=7.6$ and 0.9 Hz, H-6), 7.59–7.71 (4H, m, Ar-H), 7.80 (1H, ddd, $J=7.6$, 7.2 and 1.5 Hz, H-7), 8.11–8.15 (2H, m, H-2′,6′) and 8.29 (1H, dd, $J=8.0$ and 1.5 Hz, H-5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 98.36 (C-3), 113.96 (C≡N), 118.28 (C-8), 122.03 (C-4a), 126.25 (C-6), 126.87 (C-5), 128.75 (C-3′,5′), 129.16 (C-2′,6′), 130.16 (C-1′), 133.34 (C-4′), 135.25 (C-7), 155.46 (C-8a), 170.84 (C-2) and 174.14 (C-4). EIMS: *m*/*z* 247(M^+). Compound **5b**: mp 169–170°C. Compound **5c**: mp 206–207°C. Compound **5d**: mp 202–203°C.
3. The product in this case was a viscous liquid which has been assigned the structure **6**. IR (ν, KBr, cm^{-1}): 2105 (azide), 1640 (flavone C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 6.06 (1H, s, H-α), 7.41 (2H, d, $J=8.4$ Hz, H-2″,6″), 7.44–7.57 (7H, m, Ar-H), 7.74 (1H, ddd, $J=8.7$, 7.5 and 1.6 Hz, H-7), 8.06 (2H, d, $J=8.7$ Hz, H-3″,5″) and 8.22 (1H, dd, $J=7.8$ and 1.5 Hz, H-5).



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