A simple conversion of \(E\)-3-benzylidene-flavanones to 3-benzoylflavones by chromic acid oxidation

Asok K Mallik* & Falguni Chattopadhyay
Department of Chemistry, Jadavpur University,
Kolkata 700 032, India
E-mail: mallikak52@yahoo.co.in

Received 2 September 2003; accepted (revised) 4 May 2005

Oxidation of \(E\)-3-benzylideneflavanones with \(\text{CrO}_3/\text{AcOH}\) yields 3-benzoylflavones in moderate yield.

**Keywords:** Benzylideneflavanones, benzoylflavones, chromic acid, oxidation

**IPC:** Int.Cl. 7 C 07 D 311/30

In connection with some other problems\(^1\) we required several trans-3-benzylflavanones \(1\). For preparation of \(1\), we chose chromic acid oxidation of 3(\(S^*\))-benzyl-4(\(S^*\))-hydroxy-2(\(S^*\))flavans \(2\) obtainable by sodium borohydride reduction\(^2\) of \(E\)-3-benzylideneflavanones \(3\). Thus, when three 3(\(S^*\))-benzyl-4(\(S^*\))-hydroxy-2-(\(S^*\))flavans \(2\) were oxidised in this way, the first two compounds gave the desired products while the last one gave trans-3-(\(p\)-methoxybenzoyl)-flavanone \(4\) (Scheme I). This observation led us to suggest that under the reaction condition the initial product \(1c\) is readily converted to the radical \(5\) (having a scope of enjoying extra stability by resonance) which is then transformed to \(4\) (ref. 3).

It was envisaged that \(E\)-3-benzylideneflavanones \(3\) on treatment with chromic acid might generate the radical \(6\) which would have the scope of enjoying extra stability like \(5\) and of transforming to 3-benzoylflavones \(7\). So, chromic acid oxidation of \(3\) might be one method for direct conversion of \(3\) to \(7\).

Thus, when the \(E\)-3-benzylideneflavanone \(3a\) was treated with \(\text{CrO}_3/\text{HOAc}\) at room temperature, the reaction was found to be slow and about four days were required for disappearance of the starting material. But on refluxing, the reaction was complete within 6 hr and under both the reaction conditions only one product was obtained. Analytical and spectroscopic data confirmed it to be 3-benzoylflavone \(7a\) (Scheme II). The study was then extended to five other \(E\)-3-benzylideneflavanones and the results are presented in Table I.

\[\text{Scheme I}\]
An interesting feature observed in the 1H NMR spectra of 3-benzoylflavones 7 is that the ortho-protons of their B-ring (H-2',6') are seen to appear at somewhat higher field as compared to the same protons of corresponding 3-unsubstituted flavones (δ 7.80-7.90). So, this would be a very simple method for direct conversion of E-3-benzylideneflavanones 3 to 3-benzoylflavones 7 and is a good addition to the methods reported earlier4-6.

Experimental Section

All melting points are uncorrected. IR spectra were recorded in KBr disc on a Perkin-Elmer 297 spectrophotometer; 1H NMR spectra in CDCl 3 on a Bruker AM-300L (300 MHz) spectrometer.

General procedure for the reaction of CrO3 with E-3-benzylideneflavanones 3: To a solution of E-3-benzylideneflavanone 3 (1 mmole) in glacial acetic acid (10 mL), a solution of CrO3 (5 mmole) in the same solvent (5 mL) was added and the resulting mixture was either kept at room temperature for 4 days or at reflux for 6 hr. It was then poured into water (100 mL) and aqueous solution of sodium metabisulphite was added to reduce Cr(VI). The resulting material was then extracted with chloroform (3 × 25 mL), washed with water, dried and concentrated. Column chromatography of the material so obtained furnished the pure products 7.

Analytical and spectral data of the products are as follows:

7a: m. p. 114-15°, IR: 1672 (C=O), 1632 (C=O) cm⁻¹; 1H NMR: δ 7.33-7.56 (7H, m, Ar-H), 7.60 (1H, br. d, J = 8.4 Hz, H-8), 7.63-7.67 (2H, m, H-2',6'), 7.77 (1H, ddd, J = 8.4, 7.8 and 1.5 Hz, H-7), 7.91-7.94 (2H, m, H-2",6"), 8.25 (1H, dd, J = 8.1 and 1.5 Hz, H-5); Found: C, 80.78; H, 4.18. C22H14O3 requires C, 80.97; H, 4.32%.

7b: m. p. 168-69°, IR: 1655 (C=O), 1615 (C=O) cm⁻¹; 1H NMR: δ 3.82 (3H, s, OCH3), 6.87 (2H, pattern resembles a pair of triplets, J = 7.2, 2.7 or 2.1 Hz, H-3",5"), 7.33-7.49 (4H, m, Ar-H), 7.59 (1H, br. d, J = 8.6 Hz, H-8), 7.66-7.69 (2H, m, H-2',6'), 7.76 (1H, ddd, J = 8.1, 7.8 and 1.5 Hz, H-7), 7.89 (2H, pattern resembles a pair of triplets, J = 6.9 and 2.1 or 2.7 Hz, H-2",6"), 8.25 (1H, dd, J = 7.8 and 1.5 Hz, H-5); EIMS m/z (rel. intensity): 356 (100, M +), 328 (84.6, M+−CO), 314 (10.0), 279 (11.1), 249 (22.3), 208 (8.1), 165 (11.5), 135 (70.7, MeO−C6H4−C≡O), 129(68.2), 107 (13.0), 92 (41.1), 77 (37.4); Found: C, 77.31; H, 4.49. C23H16O4 requires C, 77.52; H, 4.53%.

7c: m. p. 161-62°, IR: 1665 (C=O), 1620 (C=O) cm⁻¹; 1H NMR: δ 3.95 (3H, s, OCH3) 6.98 (1H, d, J = 2.4 Hz, H-8), 7.03 (1H, dd, J = 8.8 and 2.4 Hz, H-6), 7.35-7.43 (5H, m, Ar-H), 7.52 (1H, t, J = 8.1 Hz, H-4"), 7.62-7.65 (2H, m, H-2',6"), 7.90-7.93 (2H, m, H-2",6"), 8.15 (1H, d, J = 9.0 Hz, H-5); Found: C, 77.31; H, 4.49. C23H16O4Cl requires C, 77.52; H, 4.53%.

7d: m. p. 169-70°, IR: 1670 (C=O), 1630 (C=O) cm⁻¹; 1H NMR: δ 2.49 (3H, s, CH3), 7.34 (2H, pattern resembles a pair of triplets, J = 8.7, 2.4 or 1.8 Hz,
H-3',5'$, 7.39 (2H, pattern resembles a pair of triplets\(^7\), \(J = 8.4\) and 1.5 or 2.4 Hz, H-3''5''), 7.48 (1H, d, \(J = 8.4\) Hz, H-8), 7.57 (2H, pattern resembles a pair of triplets\(^7\), \(J = 8.7\) and 1.5 or 2.4 Hz, H-2',6'), 7.58 (1H, dd, \(J = 8.1\) and 2.1 Hz, H-7), 7.85 (2H, pattern resembles a pair of triplets\(^7\), \(J = 8.7\) and 2.4 or 1.5 Hz, H-2'',6''), 8.00 (1H, br. s, H-5); Found: C, 67.55; H, 3.64. C\(_{23}\)H\(_{14}\)O\(_3\)Cl\(_2\) requires C, 67.49; H, 3.45%.

7f: m.p. 166-67\(^\circ\), IR: 1665 (C=O), 1620 (C=O) cm\(^{-1}\); \(^1\)H NMR: \(\delta\) 7.32-7.71 (8H, m, Ar-H), 7.90 (2H, d, \(J = 7.8\) Hz, H-2''6''), 8.19 (1H, d, \(J = 2.7\) Hz, H-5); Found: C, 61.15; H, 2.54. C\(_{22}\)H\(_{11}\)O\(_3\)Cl\(_3\) requires C, 61.49; H, 2.58%.

Acknowledgements

The authors are thankful to the authorities of IICB, Kolkata and RSIC, CDRI, Lucknow for \(^1\)H NMR and mass spectral measurements and to the UGC, New Delhi for financial assistance.

References