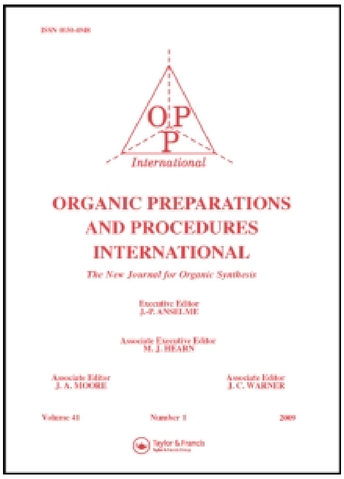

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A CONVENIENT METHOD FOR THE SYNTHESIS OF FLAVANONES BY THE SELECTIVE OXIDATION OF FLAVAN-4-OLS WITH HYPERVALENT IODINE

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A CONVENIENT METHOD FOR THE SYNTHESIS OF FLAVANONES by the SELECTIVE OXIDATION OF FLAVAN-4-OLS with HYPERVALENT IODINE

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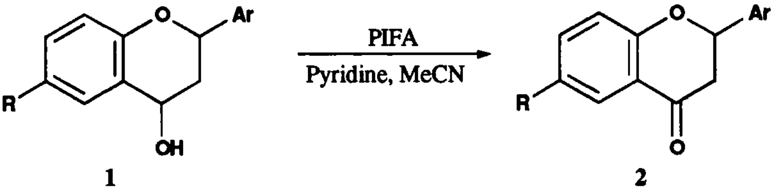
The oxidation of flavan-4-ols with dimethyl sulfoxide[1] and sodium dichromate[2] has been reported to produce flavanones whereas with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) flavones are formed along with flavanones as minor products.[3] Phenyliodo *bis*(trifluoroacetate) (PIFA) is a powerful dehydrogenating agent[4] and most reactions proceed under mild conditions. These observations, coupled with our continued interest in flavonoids[5] and hypervalent iodine chemistry,[6] prompted the use of PIFA for the oxidation of flavan-4-ols (**1a-g**).

Treatment of flavan-4-ol (**1a**) with an equimolar amount of PIFA in refluxing acetonitrile for 4 hrs resulted in the exclusive formation of the flavanone (**2a**). Addition of pyridine to the reaction mixture reduced the reaction time from 4 hrs to 1 hr. The generality of this transformation was checked by converting different flavan-4-ols (**1b-g**) to flavanones (**2b-g**) with PIFA in presence of pyridine. The use of two equivalents of PIFA in acetonitrile afforded a mixture of flavanone, flavone and isoflavone as indicated by ^1H NMR spectrum of reaction mixture. However, in presence of pyridine only flavanones were obtained even when two equivalents of PIFA was used and further oxidation of flavanones did not occur as recently reported using hypervalent iodine[7] and DDQ.[3]



In conclusion, the present oxidative conversion of **1** to **2** offers a selective, convenient and mild method for the synthesis of flavanones in high yields.

EXPERIMENTAL SECTION

Melting points were determined in a sulfuric acid bath in open capillaries and are uncorrected. IR spectra were recorded on a Perkin-Elmer 842 IR spectrophotometer in Nujol mulls and ^1H NMR spectra on a Perkin-Elmer R-32 machine using $CDCl_3$ as the solvent and TMS as an internal standard. Flavan-4-ols were obtained directly from 2'-hydroxychalcones by reductiver cyclization with sodium borohydride in presence of sodium hydroxide.[14]

TABLE: Oxidation of flavan-4-ols (1) to Flavanones (2)

Products		Yield (%)	mp. (°C)	lit. mp. (°C)
2a	R = H, Ar = C_6H_5	90	75-76	75 [8]
2b	R = H, Ar = 4-$MeOC_6H_4$	92	88-89	88-89[9]
2c	R = Cl, Ar = C_6H_5	92	96-97	96-97[10]
2d	R = Cl, Ar = 4-$MeOC_6H_5$	94	106-7	106-7[11]
2e	R = Cl, Ar = 4-ClC_6H_4	92	134-35	134-35[12]
2f	R = Me, Ar = C_6H_5	95	104-5	105 [13]
2g	R = Me, Ar = 4-$MeOC_6H_4$	94	108-9	108-10[13]

General Procedure.- A mixture of flavan-4-ol (**1a**, 0.226 g, 1 mmol), phenyliodo *bis*(trifluoroacetate) (0.460 g, 1.1 mmol) and pyridine (0.158 g, 2 mmol) in acetonitrile (20 mL) was refluxed for 1 hr. Most of the solvent was distilled off. Water (50 mL) was added and the mixture was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic extract was washed with $NaHCO_3$ solution (2 x 20 mL) followed by water and dried (Na_2SO_4). The solvent was distilled off and residue was chromatographed over silica gel 'G' [elution with ethyl acetate hexane (1:19)] to afford 0.202 g (90%) of **2a** as colorless prisms, mp. 75-76° lit.[8] mp. 75°.

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