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Regioselective Synthesis of Methyl 2,3-Dihydro-2-aryl Benzofuran-3-Carboxylates Using Thallium(III) Nitrate

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### REGIOSELECTIVE SYNTHESIS OF METHYL 2,3-DIHYDRO-2-ARYL BENZOFURAN-3-CARBOXYLATES USING THALLIUM(III) NITRATE

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Flavanones (1a-d) undergo smooth ring contraction Abstract: nitrate in of perchloric thallium(III) presence resulting the formation of trimethyl orthoformate in methyl 2.3-dihydro-2-arylbenzofuran-3-carboxylates The mechanism of this oxidation has also in good yields. been discussed.

variety oxidative rearrangement of The olefins and carbonyl compounds using thallium(III) nitrate (TTN) has been reported  $^{1-3}$ . In continuation of our earlier fla vones4 to studies on the oxidation of flavanones isoflavones<sup>5,6</sup> using thallium(III) salts, we report herein a regioselective ring contraction of flavanones (1a-d) using thallium(III) nitrate in trimethyl orthoformate (TMOF) in presence of 70% perchloric acid.

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$$\begin{array}{c|c}
R^{1} & & & \\
R & & & \\
\hline
 & & & \\$$

1 - 3

a; 
$$R=R^1 = H$$
;  $Ar = C_6 H_5$ 

b; 
$$R=CH_3$$
;  $R^1=H$ ;  $Ar=C_6H_5$   
c;  $R=CI$ ;  $R^1=CH_3$ ;  $Ar=C_6H_5$ 

c; R=C1; R<sup>1</sup>=CH<sub>3</sub>; Ar= 
$$C_6H_5$$

d; 
$$R=R^1=H$$
;  $Ar=3-NO_2C_6H_4$ 

#### Scheme I

Thus, the treatment of 1a with thallium(III) nitrate in trimethyl orthoformate in presence of 70% perchloric acid at room temperature afforded 2a and a little amount flavones 3a (in approximately 75% 15% and respectively).

generality of this transformation was established by treating other substituted flavanones (1a-d), similar conditions when 2b-d [contaminated under little amount of flavone (3b-d) were formed in good yields (Scheme I). All compounds were separated by column chromatography, characterized by IR and <sup>1</sup>H NMR spectral data and are listed in Table I.

Yields are based upon the isolated pure oily products (column chromatography).

(a) (b)

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Table I: Oxidation of 1 to 2 using TTN

Products <sup>a</sup>	Yield <sup>b</sup>	IR(nujol) cm <sup>-1</sup>	<sup>1</sup> H NMR (CDCI <sub>3</sub> )
2a	75	1740	$3.78(s, 3H, -COOCH_3)$ , $4.25(d, 1H, C_3-H), 6.10(d, 1H, C_2-H)$ , $6.80-7.70$ (m, $9H, aromatic protons$ ).
2b	76	1737	$2.22(s,3H,C_5-CH_3),3.72(s,3H,-COOCH_3)$ , $4.10(d,1H,C_3-H)$ , $5.96(d,1H,C_2-H)$ , $5.60-7.54(m,8H,aromatic protons)$ .
2c	72	1740	2.30(s,3H, $C_6$ - $CH_3$ ), 3.76(s,3H,- $COOCH_3$ ) 4.15(d, 1H, $C_3$ -H), 6.07(d,1H, $C_2$ -H),7.10-7.60(m,7H,aromatic protons).
2d	73	1740	$3.78(s, 3H, -COOCH_3), 4.15(d, 1H, G_3-H), 6.12(d, 1H, C_2-H), 6.70-8.21(m, 8H, aromotic protons).$
(a)	(a) Flavones 3 are al	lso formed as bypro	ones 3 are also formed as byproducts (10-20%) in all the cases.

A probable mechanism (scheme II) of this transformation may involve the electrophilic attack of thallium (III) nitrate on enol ether  $\underline{5}$  (formed by the loss of methanol from initially formed flavanone dimethylacetal  $\underline{3}$ ) resulting in the formation of the intermediate  $\underline{6}$ . Subsequent aryl migration with concomitant cleavage of the weak carbon-thallium bond may result in the formation of  $\underline{2}$  (path  $\underline{a}$ ). In a competing pathway (path  $\underline{b}$ ), the reductive cleavage of carbon-thallium bond may be assisted by the loss of  $C_2$ -H to afford  $\underline{3}^7$ .

In conclusion it may be added that the present oxidative approach is quite convenient for the synthesis of  $\underline{2}$ 

$$\frac{1}{1} \xrightarrow{\frac{1 \text{MOF}}{\text{HCIO}_4}} \xrightarrow{R^1} \xrightarrow{R^1} \xrightarrow{OMe} \xrightarrow{R^1} \xrightarrow{OMe} \xrightarrow{OMe} \xrightarrow{ONO_2} \xrightarrow{ONO$$

#### **Experimental**

Melting points were determined in sulphuric acid bath in open capillaries and are uncorrected. IR spectra were recorded in nujol mulls on Perkin-Elmer 842 IR and <sup>1</sup>H NMR spectra were scanned on Perkin-Elmer R-32 machine using CDCl<sub>3</sub> as solvent and TMS as an internal standard.

All flavanones were prepared by acid catalyzed cyclization of  $\underline{o}$ -hydroxychalcones<sup>8</sup>. Thallium(III) nitrate was purchased from Aldrich chemical company, USA.

## Oxidation of 1 with Thallium(III) nitrate in Acidic Trimethyl orthoformate: General Procedure

trimethyl orthoformate (TMOF; 20 ml) was added perchloric acid (0.03 mol) with stirring. To the resulting mixture was added thallium(III) nitrate (TTN; 0.011 mol). The contents, after stirring at room temperature for 20-30 min, were diluted with  $\mathrm{CH_2Cl_2}$  (20 ml). The precipitated thallium (I) salt was filtered off and washed with  $\mathrm{CH_2Cl_2}$  (50 ml). The filtrate was washed with aqueous  $\mathrm{NaHCO_3}$  (2x50 ml), followed by water and dried  $\mathrm{(Na_2SO_4)}$ . The solvent was distilled off at reduced pressure. The residue so obtained was separated by passing through a column of silica gel 'G' using Hexane: ethylacetate as eluent (Table I).

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