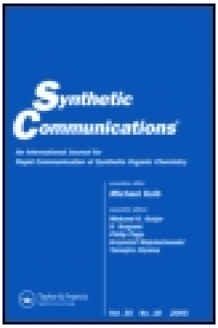

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Regioselective Synthesis of Methyl 2,3-Dihydro-2-aryl Benzofuran-3-Carboxylates Using Thallium(III) Nitrate

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

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

The oxidative rearrangement of a variety of olefins and carbonyl compounds using thallium(III) nitrate (TTN) has been reported[1-3]. In continuation of our earlier studies on the oxidation of flavanones to flavones[4] and isoflavones[5,6] 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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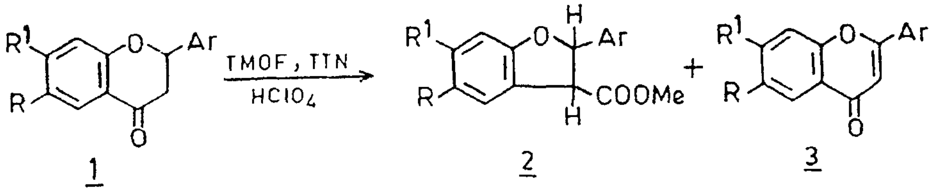


1-3

a; $R=R^1=H$; $Ar = C_6H_5$
b; $R=CH_3$; $R^1=H$; $Ar= C_6H_5$
c; $R=Cl$; $R^1=CH_3$; $Ar= C_6H_5$
d; $R=R^1=H$; $Ar= 3\text{-}NO_2C_6H_4$

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 of flavones 3a (in approximately 75% and 15% yield, respectively).

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

Table I: Oxidation of 1 to 2 using TTN

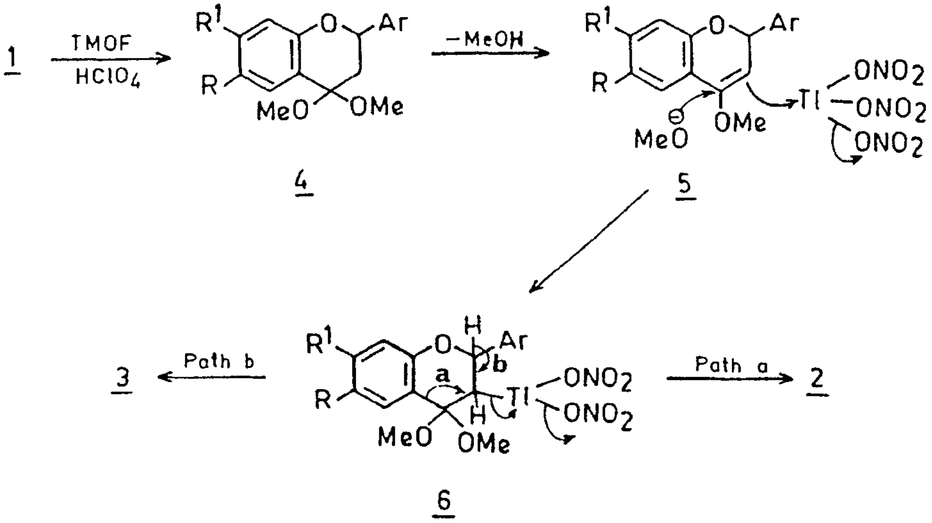
Products[a]	Yield[b] %	IR(nujol) cm^{-1}	^1H NMR ($CDCl_3$) δ
2a	75	1740	3.78(s,3H,-$COOCH_3$), 4.25(d,1H,C_3-H),6.10(d, 1H,C_2-H), 6.80-7.70(m,9H,aromatic protons).
2b	76	1737	2.22(s,3H,C_5-CH_3),3.72(s,3H,-$COOCH_3$), 4.10(d, 1H,C_3-H), 5.96(d,1H,C_2-H), 5.60-7.54(m,8H, aromatic protons).
2c	72	1740	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,C_3-H), 6.12(d,1H, C_2-H), 6.70-8.21(m,8H,aromotic protons).

(a) Flavones 3 are also formed as byproducts (10-20%) in all the cases.

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

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

In conclusion it may be added that the present oxidative approach is quite convenient for the synthesis of 2



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 ^1H NMR spectra were scanned on Perkin-Elmer R-32 machine using $CDCl_3$ as solvent and TMS as an internal standard.

All flavanones were prepared by acid catalyzed cyclization of o-hydroxychalcones[8]. Thallium(III) nitrate was purchased from Aldrich chemical company, USA.

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

To a solution of flavanone (1; 0.01 mol) in 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 CH_2Cl_2 (20 ml). The precipitated thallium (I) salt was filtered off and washed with CH_2Cl_2 (50 ml). The filtrate was washed with aqueous $NaHCO_3$ (2x50 ml), followed by water and dried (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).

Acknowledgements

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