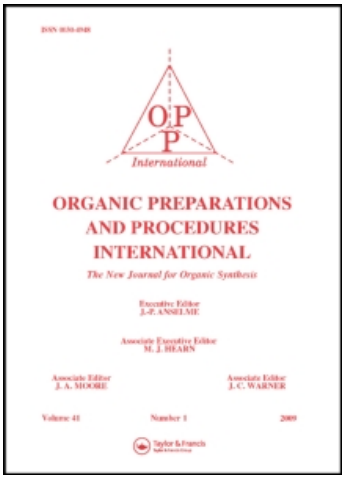

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OXIDATION OF FLAVANONES WITH LEAD TETRAACETATE, TRIMETHYL ORTHOFORMATE AND PERCHLORIC ACID

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OXIDATION OF FLAVANONES WITH LEAD TETRAACETATE, TRIMETHYL ORTHOFORMATE AND PERCHLORIC ACID

Submitted by (07/06/93)

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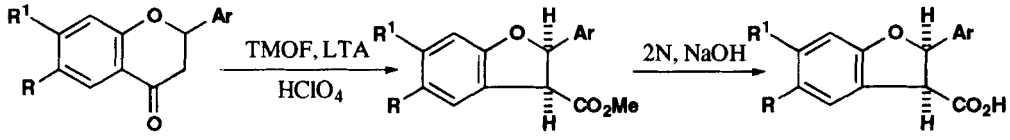
Recently, lead tetraacetate (LTA) convert acetophenones and α-tetralones smoothly into methyl arylacetates and indane-1-carboxylates respectively.[1] The present communication reports a facile one-step conversion of flavanones (**1**) into *cis*-methyl-2,3-dihydro-2-arylbenzofuran-3-carboxylates (**2**) in excellent yields. Alkaline hydrolysis of **2** afforded the corresponding acid **3**, whose *cis*-stereochemistry was established on the basis of the ^{1}H NMR spectra.[2]



1 **2** **3**

The generality of this transformation was demonstrated by the conversion of other flavanones (**1b-e**) into **2b-e** in good to excellent yields. All compounds were purified by column chromatography and characterized by IR and ^{1}H NMR spectral data (Table).

In analogy with our earlier proposed mechanism,[3] the reaction may involve the electrophilic attack of lead tetraacetate on enol ether *anti* to C_2-aryl ring (formed *in situ* by the loss of methanol

from initially formed flavanone dimethyl acetal **4**) resulting in the formation of intermediate **5**. Subsequent aryl migration from the *back side* with concomitant cleavage of the weak C-Pb bond would result in the formation of **2**.

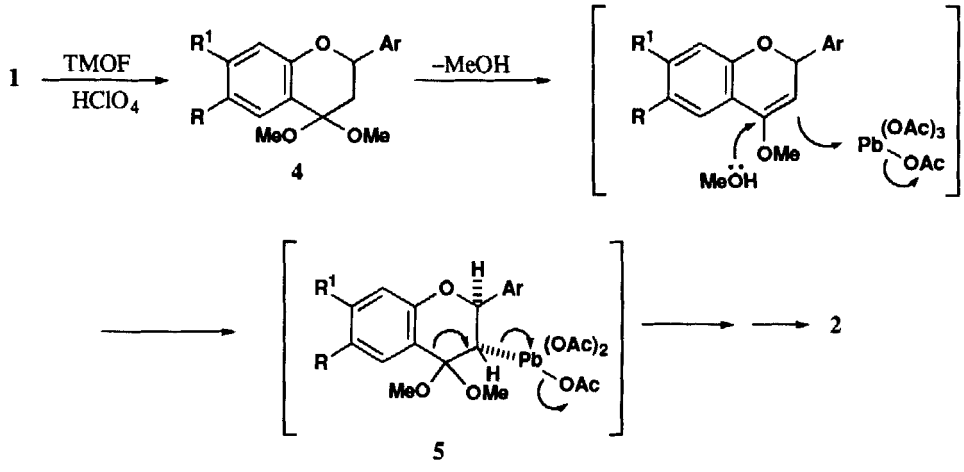


TABLE. Oxidation of **1** to **2** and **3** with LTA

Products	Yield[a] (%)	mp. (°C)	Analysis (%) Found C	(Cal.) H
2a; $R = R^1 = H$; $Ar = C_6H_5$	85	c	–	–
2b; $R = CH_3$; $R^1 = H$; $Ar = C_6H_5$	86	c	–	–
2c; $R = CH_3$; R^1 =Cl; $Ar = C_6H_5$	82	c	–	–
2d; $R = R^1 = H$; $Ar = 3\text{-}NO_2C_6H_4$	80	c	–	–
2e; $R = R^1 = H$; $Ar = 4\text{-}ClC_6H_4$	70	oil[d]	–	–
3a; $R = R^1 = H$; $Ar = C_6H_5$	70[b,d]	88-89	75.04 (75.00)	4.58 (5.00)
3b; $R = CH_3$; $R^1 = H$; $Ar = C_6H_5$	70[b,d]	120-121	75.00 (75.59)	5.48) (5.51)

a) Yields are based on the pure products obtained through the column chromatography. b) Yields are based upon the isolated solid products. c) Oily products, having superimposable IR and ^1H NMR (ref. 3) spectral data. d) Satisfactory spectral data (IR and ^1H NMR) were obtained.[2]

In conclusion, the present procedure provides a rapid and convenient route for the synthesis of **2** and **3** and avoids the use of highly toxic thallium(III) salts.[3]

EXPERIMENTAL SECTION

Melting points were determined in Thiele tube (sulfuric acid bath) in open capillaries and are uncorrected. IR spectra were recorded in nujol mulls on Perkin-Elmer 842 IR and ^1H NMR were scanned on Perkin-Elmer R-32 instrument using $CDCl_3$ as solvent and TMS as an internal standard.

***cis*-Methyl 2,3-Dihydro-2-arylbenzofuran-3-carboxylate (2). General Procedure.**- To a solution of flavanone (**1a**, 0.001 mol) trimethyl orthoformate (15 mL) and 70% perchloric acid (0.2 mL, 0.002 mol) was added lead tetraacetate (0.0011 mol) in one portion. The resulting solution was stirred at room temperature for 1-2 hrs (the progress of reaction was monitored by TLC). The solvent was then distilled under reduced pressure and the residue triturated with CH_2Cl_2 (50 mL). The solid so obtained was filtered off and the filtrate was washed with water (2x50 mL) and dried ($MgSO_4$). The solvent was distilled off *in vacuo* and the residual mass was purified by passing through a column (2 ft.) of silica gel 'G' (50 g) using hexane (200 mL) as eluent (Table).

***cis*-2,3-Dihydro-2-arylbenzofuran-3-carboxylic Acid (3). General Procedure.**- A mixture of 2 (0.001 mol) and aqueous 2N NaOH (10-15 mL) was heated at reflux for 5-6 hrs (until the reaction mixture became clear). The reaction mixture was then extracted with CH_2Cl_2 (2x50 mL). The aqueous layer was acidified with conc. HCl and extracted again with CH_2Cl_2 (2x50 mL) and dried ($MgSO_4$). The solvent was evaporated from the combined organic layers under reduced pressure and the gummy mass obtained was triturated with hexane to afford **3** as solids (Table).

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2. **Compound 2e**: IR (nujol): 1730 cm^{-1} (C=O, ester); ^1H NMR ($CDCl_3$); δ 3.76 (s, 3H, $-CO_2CH_3$), 4.25 (d, 1H, C_3-H) J = 8.5 Hz), 6.05 (d, 1H, C_2-H, J = 8.5 Hz), 6.80-7.40 (m, 8H, Ar-H). **Compound 3a**: IR (nujol): 3300-3000 cm^{-1} (O-H, acid), 1710 cm^{-1} (C=O, acid). ^1H NMR ($CDCl_3$): δ 4.25 (d, 1H, C_3-H, J = 8.5 Hz), 6.05 (d. 1H. C_2-H, J = 8.5 Hz). 7.0-7.70 (m, 10H, Ar-H and C_3-CO_2H). **Compound 3b**: IR (nujol): 3300-3000, cm^{-1} (O-H, acid), 1715 cm^{-1} (C=O, acid). ^1H NMR ($CDCl_3$): δ 2.29 (s, 2H, C_5-CH_3) 4.23 (d, 1H, C_3-H, J = 8.5 Hz), 6.05 (d, 1H, C_2-H J = 8.5 Hz), 6.80-7.70 (m, 9H, Ar-H and C_3-CO_2H).

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