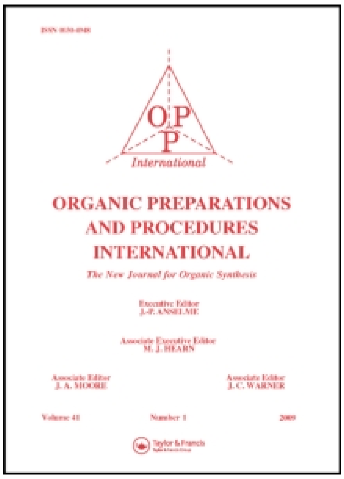

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SIMPLE AND FACILE OXIDATION OF ALDEHYDES TO CARBOXYLIC ACIDS

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SIMPLE AND FACILE OXIDATION OF ALDEHYDES TO CARBOXYLIC ACIDS

Submitted by B. Ramesh Babu[†] and K. K. Balasubramaniam*[††]
(06/14/93)

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We needed an efficient and practical method for the large scale oxidation of unsaturated aldehydes, phenolic aldehydes, aminobenzaldehyde and pyrrole-2-carboxaldehyde to the corresponding acids. Though numerous reagents and methods are described in literature,[1-5] none of these was suitable for the oxidation of 4-(dimethylamino)benzaldehyde, 4-hydroxybenzaldehyde, and pyrrole-2-carboxaldehyde, which are very sensitive to the oxidative conditions. In most of the known methods the major disadvantages are complex operating conditions, low-conversions, and expensive reagents. The method of Dalcanale and Montanari[6] for the oxidation of aldehydes to carboxylic acids based on sodium chlorite-H_2O_2 was found to be excellent for the oxidation of simple aromatic aldehydes. However, this procedure was quite unsatisfactory and afforded tarry products and chlorinated compounds in the case of crotonaldehyde, 4-hydroxybenzaldehyde, and 4-(dimethylamino)benzaldehyde. We herein describe a simple and practical method for the oxidation of aldehydes to carboxylic acids using sodium chlorite-aqueous acetonitrile.

This procedure proved satisfactory even in the sensitive cases of unsaturated aldehydes (entries 2 and 3), phenolic aldehydes (entries 4 and 5), aminobenzaldehyde (entry 9) and heterocyclic aldehydes (entries 10 and 11). Esteban[7] reported the oxidation of an aliphatic aldehyde (entry 1) with sodium chlorite in the presence of aqueous H_2NSO_3H to give the corresponding carboxylic acid in 77% yield. However, the generality of this method and particularly its utility for the oxidation of sensitive aldehydes were not discussed. The present $NaClO_2$-aqueous acetonitrile combination is superior to existing methods in terms of operation, yield and adaptability to large scale.

The reactions were carried out by the slow addition of 1.0-1.4 equiv. of $NaClO_2$ to a solution of 1.0 equiv. of aldehyde in aqueous acetronitrile at 5-10°. In most cases, the yields were high and the products were acceptably pure.

TABLE. Oxidation of Aldehydes by Sodium Chlorite to Carboxylic Acids.

Entry	Aldehyde	Mole Equiv. of NaClO$_2$	Yield (%)	mp (lit.)^b (°C)		IR C=O (cm^{-1})
1	4-(Me$_2$)CHCH$_2$C$_6$H$_4$CH(Me)CHO	1.2	95	74-75	(75-77)	1719
2	C$_6$H$_5$CH=CHCHO	1.2	93	130-132	(133-134)	1686
3	CH$_3$CH=CHCHO	1.3	80	71-73	(72-74)	1719
4	4-HOC$_6$H$_4$CHO	1.3	50	211-213	(210-212)	1681
5	3,4-(MeO)(OH)C$_6$H$_3$CHO	1.1	85	210-211	(210-212)	1681
6	3,4-(MeO)$_2$C$_6$H$_3$CHO	1.3	92	176-178	(179-182)	1676
7	2,5-(MeO)$_2$C$_6$H$_3$CHO	1.2	75	74-76	(76-78)	1730
8	3,4,5-(MeO)$_3$C$_6$H$_2$CHO	1.2	90	167-170	(168-171)	1681
9	4-(Me$_2$N)C$_6$H$_4$CHO	1.1	89	238-240	(241-243)	1681
10	Furan-2-carboxaldehyde	1.2	90	130-131	(131-134)	1686
11	Pyrrole-2-carboxaldehyde	1.5	87	203-205	(204-208)	1718

a) One equiv. of aldehyde was used in all cases. b) Crude products. Lit. mp. or bp. data[8,9] are given in parenthesis.

EXPERIMENTAL SECTION

General Procedure for Oxidation of Aldehydes.- A solution of (0.10-0.14 mole) of sodium chlorite in 100 mL of water was added dropwise in one hr to a stirred mixture of aldehyde (0.10 mole) (99% purity) in 50-100 mL of acetonitrile. Temperature was maintained at 10° or below for 2 hrs and the reaction mixture was then stirred at room temperature for another 3 hrs. Then 10% sodium hydroxide solution (100 mL) was added and the resulting reaction mixture was extracted with ether(3x50 mL). The separated aqueous solution was cooled in an ice-bath and acidified (pH 2-3) with cold dilute hydrochloric acid. The separated solid was collected, dried and recrystallized from a suitable solvent to give the pure carboxylic acid (TLC and GC).

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

Submitted by (07/06/93)

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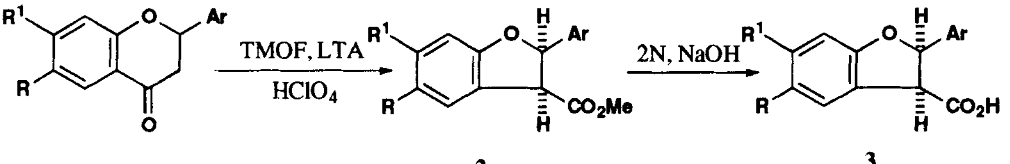
Recently, lead tetraacetate (LTA) convert acetophenones and α-tetralones smoothly into methyl arylacetates and indane-1-carboxylates respectively.[1] The present communication reports a facile one-step conversion of flavanones (**1**) into *cis*-methyl-2,3-dihydro-2-arylbenzofuran-3-carboxylates (**2**) 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