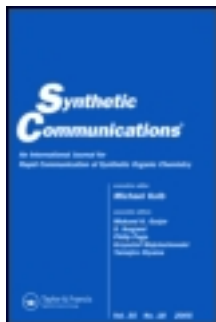


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SELENIUM(IV) OXIDE CATALYZED OXIDATION OF
ALDEHYDES TO CARBOXYLIC ACIDS WITH
HYDROGEN PEROXIDE

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Abstract: A convenient method for oxidative transformation of aromatic, hetero-aromatic and aliphatic aldehydes into carboxylic acids is presented. It is based on the oxidation of aldehydes in THF using 30% hydrogen peroxide in the presence of 5 molar % of selenium(IV) oxide. The scope and limitation of the method are discussed.

Oxidation of aldehydes to carboxylic acids is one of the fundamental reaction in organic chemistry. It is carried out with many oxidizing agents but the most popular ones, such as potassium permanganate in acid, basic and neutral solution, chromic acid, bromine, fuming nitric acid, and Jones reagent are not attractive because of environmental restrictions.¹⁻³ Actually, one of the most attractive oxidant is hydrogen peroxide, cheap and environmentally friendly reagent which can be used in both laboratory and industrial scale. Unfortunately,

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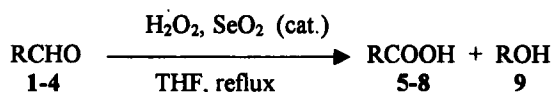
hydrogen peroxide itself is inactive toward most of aldehydes, particularly aromatic ones, and for their oxidation suitable catalyst must be used.^{4,5} Moreover, in many cases oxidation of aromatic aldehydes results in obtaining of carboxylic acid or phenol formates since two competitive reactions can take place.⁶

Ten years ago, it was found in our laboratory that hydrogen peroxide in the presence of 2,4-dinitrobenzeneseleninic acid oxidizes aromatic aldehydes, having electron-donating substituents, to phenol formates by the Baeyer-Villiger rearrangement⁷. More recently, similar results were reported when selenium(IV) oxide was used as the catalyst.⁸ On the other hand, it has been known that aromatic as well as aliphatic aldehydes treated with hydrogen peroxide in the presence of benzeneseleninic acid produced carboxylic acids, mostly in fair yields.⁹

In this work, hydrogen peroxide oxidation of aromatic, heteroaromatic, and aliphatic aldehydes in the presence of various selenium compounds was reinvestigated. It was found that for conversion of aldehydes 1-4 into carboxylic acids 5-8 the most effective catalyst was easily available and cheap selenium(IV) oxide. Only in few particular cases the reaction runs also to phenols 9.

The reaction was carried out in tetrahydrofuran under reflux¹⁰. Commercial 30% hydrogen peroxide was used in two-fold molar excess in the presence of 5 mol % of selenium(IV) oxide. After the reaction was finished, the mixture was analysed using gas chromatography, and products were identified by GC/MS. Moreover, in the most cases produced acids were isolated preparatively. The

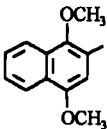
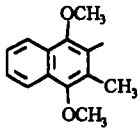
results are presented in Tables 1-4. The selected examples (acids **5a**, **5e**, **7a**, **8c**) shown that the method is useful in molar scale.



Oxidation of aromatic aldehydes having no substituents (**1a**, **b**) or these ones bearing methyl group (**1k**, **1l**) lead to corresponding carboxylic acids (**5a**, **b**, **k** and **l**). Similar results were found for aromatic aldehydes having one or two electron-withdrawing groups (**1c-1j**), although for disubstituted ones (**1f**, **g**) the reaction proceeded more slowly. In all these cases, arenecarboxylic acids were isolated in the yields of above 83 %. Even benzaldehydes (**1m**, **o**) having the electron-donating methoxy group in ortho or para position (**1m**, **o**) produced substantial amounts (44-46 %) of acids (**5m**, **o**) beside of phenols (**9m**, **o**), contrary to the earlier works where phenols were reported as sole products.^{7,8} 3-Methoxybenzaldehyde (**1n**) was oxidized exclusively to carboxylic acid (**5n**). When two electron-donating methoxy groups were present in the aromatic ring of aldehydes (**1p-1s**), phenols (**9p-9s**) were the major products or, as in the case of aldehyde **1s**, formation of acid **5s** formation was not observed. In some cases, hydroxy-1,4-quinones, resulting from oxidation of the aromatic ring, were also identified as the by-products (Table 1).

Oxidation of aromatic dialdehydes (**2a-c**) resulted in production of dicarboxylic acids (**6a-c**) in 80-93 % yields, although the reaction time had to be

Table 1. Oxidation of aromatic aldehydes 1

1	Aldehyde	Reaction time, h	Products, yield, ^a %	
			Acids 5	Phenols 9
a	C ₆ H ₅	2.5	97 (96)	98 ^b
b	1-naphthyl	7	82 (86)	- ^c
c	2-ClC ₆ H ₄	9	97 (98)	-
d	3-ClC ₆ H ₄	6	93 (98)	-
e	4-ClC ₆ H ₄	6	83 (98)	98 ^b
f	2,4-Cl ₂ C ₆ H ₃	18	94 (97)	-
g	2,6-Cl ₂ C ₆ H ₄	52	86 (93)	- (4)
h	4-CNC ₆ H ₄	5	99 (97)	-
i	4-NO ₂ C ₆ H ₄	3	87 (99)	-
j	4-CH ₃ OOC ₆ H ₄	5	95 (98)	-
k	2-CH ₃ C ₆ H ₅	10	88 (89)	(9)
l	4-CH ₃ C ₆ H ₅	7	88 (96)	-
m	2-CH ₃ OC ₆ H ₄	24	44 (46)	49 (49) ^d
n	3-CH ₃ OC ₆ H ₄	24	96 (98)	-
o	4-CH ₃ OC ₆ H ₄	24	46 (47)	41 (38) ^e
p	2,5-(CH ₃ O) ₂ C ₆ H ₃	24	24 (24)	40 (68) ^f
q	3,4-(CH ₃ O) ₂ C ₆ H ₃	24	21 (21)	76
r		96	22 (23)	55 ^B
s		48	- (-)	(81) ^h

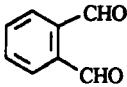
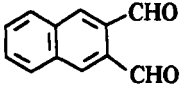
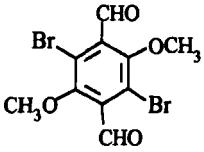
^aIsolated yields. Data in parentheses are referred to yields determined by GC.

^bYield for molar scale. ^c1,4-Epoxynaphthalene (6 %). ^d2-Formyloxyanizole (2%).

^e1,4-Benzoquinone (13 %). ^f2,5-dimethoxy-1,4-benzoquinone (19 %).

^g2-Hydroxy-1,4-naphthoquinone (8 %). ^h2-Hydroxy-3-methyl-1,4-naphthoquinone (5 %).

Table 2. Oxidation of aromatic dialdehydes **2**

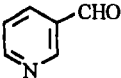
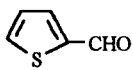
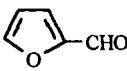
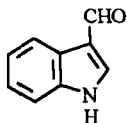
2	Aldehyde	Reaction time, h	Dicarboxylic acids 6 yield ^a , %
a		50	93
b		50	96
c		120	80

^aIsolated yields

prolonged (Table 2). Oxidation of heteroaromatic aldehyde **3a** having electron-deficient pyridine ring as well as of aldehydes having the electron-excess rings **3b** and **3c** led to the corresponding carboxylic acids **7a-d** in satisfactory to good yields (Table 3). The exception was 3-indolecarboxaldehyde (**3d**) which produced tarry mixture of several products since the pyrrole ring is very sensitive toward oxidation.

Aliphatic aldehydes **4a-f** undergone oxidation to carboxylic acids **8a-f** substantially faster than aromatic and heteroaromatic aldehydes **1-3**. The yields of

Table 3. Oxidation of heteroaromatic aldehydes **3**

3	Aldehyde	Reaction time, h	Acid 7 yield ^a , %
a		5	86 (86) 85 ^b
b		72	88 (99)
c		80	73 (62)
d		22	- (-)

^aIsolated yields. Data in parentheses are referred to yields determined by GC.

^bYield for molar scale.

acids **8** were high to excellent (Table 4), better than these reported when benzeneseleninic acid was used as the catalyst.⁹

Experimental

The reaction products presented in Tables 1-4 were analysed using Hewlett-

Table 4. Oxidation of aliphatic aldehydes 4

4	Aldehyde	Reaction time, h	Acids 8 yield ^a , %
a	CH ₃ CH ₂ CHO	3	87 (92)
b	(CH ₃) ₂ CHCHO	4	80 (80)
c	(CH ₃) ₂ CHCH ₂ CHO	3	91 (98) 89 ^b
d	CH ₃ (CH ₂) ₄ CHO	3	88 (90)
e	CH ₃ (CH ₂) ₆ CHO	3	91 (85)
f	CH ₃ (CH ₂) ₈ CHO	4	100

^aIsolated yields. Data in parentheses are referred to yields determined by GC.

^bYield for molar scale.

Packard 5890/II apparatus with capillary column HP-1 (25 m, 0.22 mm). The products were identified by comparison of their MS spectra (Hewlett-Packard 5971A) with data reported in the library NBS 49K and 75K, of their melting points (Digital Melting Point Apparatus Electrothermal IA 91100) and by analysis of their ¹H-NMR data (CDCl₃ or DMSO, TMS, Bruker DRX 300 spectrometer). Hydrogen peroxide (30%), selenium(IV) oxide and aldehydes **1a-q**, **2a, b**, **3a-d**, **4a-f** were purchased from Aldrich and Fluka. Other aldehydes were obtained according to the procedure reported in ref.¹¹ (**1p-1s**) or were delivered by Prof. Dr. Ludwik Syper (**1q**, **1r**, **2c**).

Oxidation of aldehydes

The solution of aldehyde **1** (5 mmol) in tetrahydrofuran (freshly distilled from LiAlH₄) (7.5 ml), 30% hydrogen peroxide (1.1 ml, 10 mmol) and selenium(IV)

oxide (0.28 g, 0.25 mmol) were stirred under reflux till the substrate disappeared. The reaction progress was controlled by TLC using dichloromethane as an eluent or by GC (reaction times are given in Tables 1-4). After the reaction was finished a pinch of Pd/asbestos (10%) was added, solvent was evaporated *in vacuo*, the residue was dissolved in the solution of 2.5% aqueous sodium hydrocarbonate and extracted with diethyl ether (3x20 ml). The organic and aqueous layers were separated. The aqueous layer was acidified with hydrochloric acid to pH 3-4 , and the resulted mixture containing carboxylic acid **5-8** was extracted with diethyl ether (3x20 ml). The extract was dried over anhydrous sodium sulfate, ether was removed *in vacuo* and the residue was a pure acid (**5a-i**, **5k-r**, **7c**, **8a-f**) or it was recrystallized from water (**6a,7b**), THF (**6b**, **7a**), THF-water (5:1) (**5j**) or chloroform-THF (10:1) (**6c**).

Phenols **9m**, **o**, **p** were isolated from the organic phase. It was evaporated *in vacuo* and the residue was dissolved in 5 % aqueous sodium hydroxide (50 ml) and acidified with hydrochloric acid to pH 3-4. The resulted mixture containing phenol was extracted with diethyl ether (20 ml) and the extract was worked up in the same manner as described for isolation of carboxylic acids.

The same method was used for the oxidation of aldehydes in larger scale. The solution of aldehyde (**1a**, **1e**, **3a**, **4c**) (0.1 mol) in THF (freshly distilled from LiAlH₄) (100 ml) and selenium(IV) oxide (0.55 g, 5 mmol) was treated with 30% hydrogen peroxide (22 ml, 0.2 mol) in the same manner as described above. After the reaction was finished a pinch of Pd/asbestos (10%) was added in order to decompose of peroxides. The solvent was evaporated *in vacuo*, water (200 ml)

was added and the crude product was filtered off. To the filtrate sodium hydrocarbonate (8 g) was added and the solution was acidified with HCl to pH 3-4, and carboxylic acid was extracted with diethyl ether (3x50 ml). The extract was dried over anhydrous sodium sulfate and ether was removed *in vacuo*. The residue recombined with crude product, recrystallized from hexane (**5a**), ethanol (**5e**), THF (**7a**) or distilled at 176°C (**8c**) gave pure acid.

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