A Convenient Oxidation of Halomethylarenes and Alcohols to Aldehydes with Dimethyl Selenoxide and Potassium Benzeneselenite

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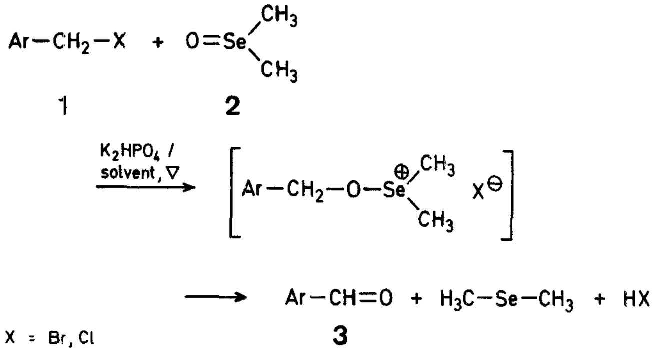
Among the various methods of preparation of aromatic aldehydes, the useful ones involve oxidation of the halomethyl substituents with 2-nitropropane potassium salt[1,2] or dimethyl sulfoxide[3,4]. However, the oxidation with 2-nitropropane salt is limited to rather simple molecules. Polysubstituted arenes or compounds bearing substituents unstable in alkaline medium, give the corresponding aldehydes only in low yields or the method does not work at all. When oxidation is carried out with dimethyl sulfoxide, very often severe reaction conditions are required, thus the usefulness of this reagent as oxidant for aromatic halomethyl derivatives is also limited[4].

It is noteworthy that diphenyl selenoxide and other aryl selenoxides were successfully used as mild oxidants for olefins, thiols, sulfides, amines, and catechols[5-9]. Dimethyl selenoxide was reported as an oxidant for olefins and some organophosphorus compounds[10]. The facile synthesis of this reagent, reported[11] by us recently, enable us now to present here different procedures to oxidize halomethyl- or hydroxymethylarenes and allylic or aliphatic alcohols to the corresponding carbonyl compounds in good yields.

The first method proposed here (Method A) is based on the assumption that dimethyl selenoxide (**2**) should oxidize the halomethyl groups in halomethylarenes **1** more easily to aldehydes **3** than dimethyl sulfoxide due to its higher nucleophilicity and on the fact that the O—Se bond is weaker than the O—S bond. The nucleophilic attack of the oxygen atom in the first step of this process and cleavage of the O—Se bond proceed more smoothly than in the case when dimethyl sulfoxide is used as an oxidant. The oxidation is carried out in the presence of potassium hydrogen phosphate to give the products in very good yields (Table 1). Use of diphenyl selenoxide instead of dimethyl selenoxide (**2**) led to lower yields or gave complex mixtures of products depending on the reactivity of the substrate.



It has also been revealed that benzeneselenic acid could be used as an oxidant for sulfides and phosphines[12]. We have now found that its potassium salt **4** can be used instead of dimethyl selenoxide as an oxidant for halomethylarenes **1** to aromatic aldehydes[3]. The reaction is carried out in acetonitrile in the presence of dipotassium hydrogen phosphate under reflux (Method B, Table 1). This oxidant has the advantage in comparison with dimethyl selenoxide (**2**), that it is a chemically stable, nonhygroscopic solid and that diphenyl diselenide (**5**) can be easily recovered in stoichiometric yield and then converted again into potassium benzeneselenite.

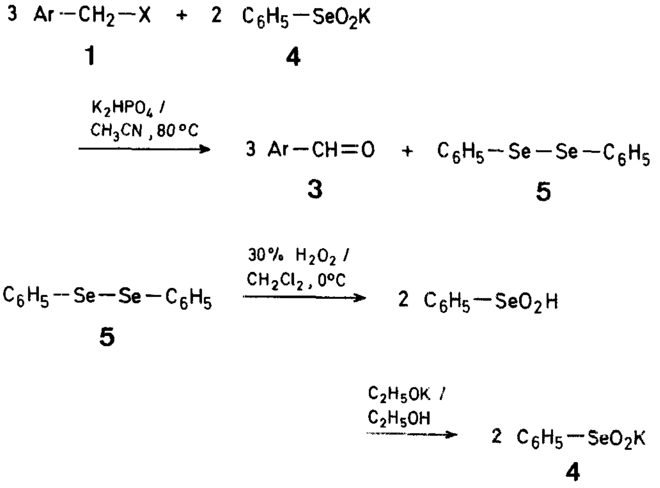


Table 1. Oxidation of Halomethyl or Hydroxymethylarenes and Alcohols with Dimethyl Selenoxide or Potassium Benzeneselenite

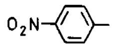
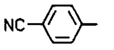
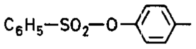
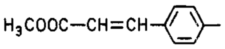
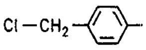
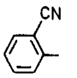
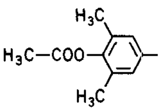
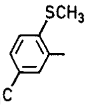
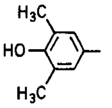
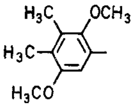
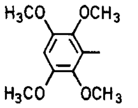
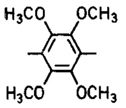
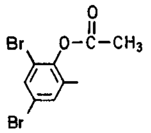
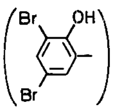
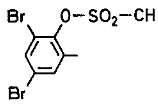
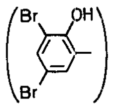
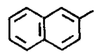
Substrate No.	Ar	X	Product	Method/solvent/ Reaction Time	Yield [%]	m.p. [°C] (solvent) or b.p. [°C]/torr	Molecular formula[a] or Lit. Data
1a		Br	3a	A/ClCH$_2$CH$_2$Cl/4h	96	106° (c-C$_6$H$_{12}$)	106°[17]
				A/CH$_3$CN/5h	100		
				A[b]/CH$_3$CN/5h	100		
1a'		Cl	3a	A[b,c]/DME/4h	98		
				A[d]/CH$_3$CN/24h	95		
1a''		OH	3a	C/C$_6$H$_6$/5h	93		
1b		Br	3b	A/ClCH$_2$CH$_2$Cl/3h	97	102° (c-C$_6$H$_{12}$)	95–96°[1,2]
1c		Br	3c	A/ClCH$_2$CH$_2$Cl/4h	97	85° (c-C$_6$H$_{12}$)	84–85°[18]
1d		Br	3d	A/ClCH$_2$CH$_2$Cl/5h	96	91° (C$_6$H$_{14}$/c-C$_6$H$_{12}$)	C$_{11}$H$_{10}$O$_3$ (190.2)
1e		Br	3e	A/ClCH$_2$CH$_2$Cl/3h	77[e]	73° (c-C$_6$H$_{12}$)	73°[19]
1f		Br	3f	A/ClCH$_2$CH$_2$Cl/3h	93	109° (c-C$_6$H$_{12}$)	108–109°[20]
1g		Br	3g	A/ClCH$_2$CH$_2$Cl/2.5h	95	79° (C$_6$H$_{14}$)	C$_{11}$H$_{12}$O$_3$ (199.2)
1h		Br	3h	A/ClCH$_2$CH$_2$Cl/2h	97	27° (C$_6$H$_{14}$)	b.p. 129–134°/3.5[21]
1i		Br	3i	A/ClCH$_2$CH$_2$Cl/0.5h	49	117° (c-C$_6$H$_{12}$)	111–112.5°[22]
1i'		OH	3i	C/C$_6$H$_6$/1.5h	80		
1j		Br	3j	A/ClCH$_2$CH$_2$Cl/6h	98	72° (C$_6$H$_{14}$)	67.5–68.5°[23]
1j'		Cl	3j	A/ClCH$_2$CH$_2$Cl/8h	98		
1k		Br	3k	A/ClCH$_2$CH$_2$Cl/24h	96	84° (c-C$_6$H$_{12}$)	84°[24]
1k'		Cl	3k	A/ClCH$_2$CH$_2$Cl/24h	88		
1l		Br, Br	3l	A/ClCH$_2$CH$_2$Cl/11h	90	141° (c-C$_6$H$_{12}$)	141°[24]
				B/CH$_3$CN/7h	83		
1m		Br	3m 	A/ClCH$_2$CH$_2$Cl/2h	77	84° (C$_6$H$_{14}$)	81–82°[25]
1n		Br	3n 	A/Cl$_2$CH$_2$CH$_2$Cl/3h	68		
1o		Br	3o	A/ClCH$_2$CH$_2$Cl/6h	98	62° (c-C$_6$H$_{12}$)	61–63°[12]
1o'		Cl	3o	A[b]/CH$_3$CN/7h	95		
				A[b]/DME/5h	93		
				B[f]/CH$_3$CN/5h	98		
				B[g]/CH$_3$CN/6h	98		
1o''		OH	3o	C/C$_6$H$_6$/5h	100		

Table 1. (continued)

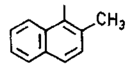
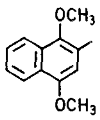
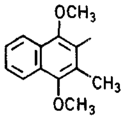
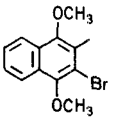
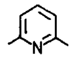
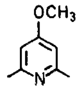
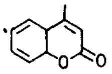
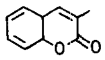
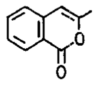
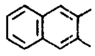
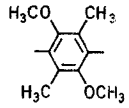
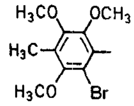
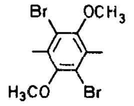
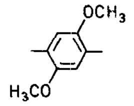
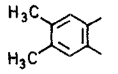
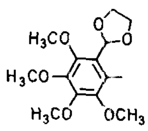
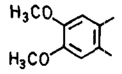
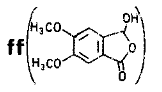
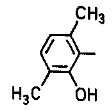
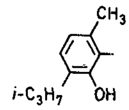
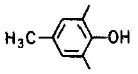
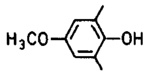
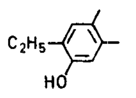
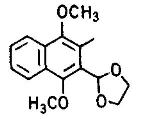
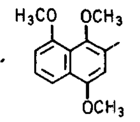
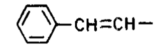
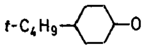
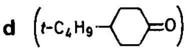
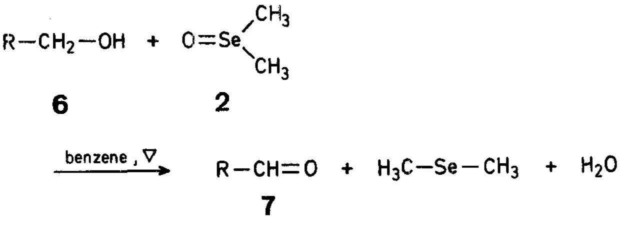
Substrate No.	Ar	X	Product	Method/solvent/ Reaction Time	Yield [%]	m.p. [°C] (solvent) or. b.p. [°C]/torr	Molecular formula[a] or Lit. Data
1p		Br	**3p**	A/ClCH$_2$CH$_2$Cl/12h	92	52° (c-C$_6$H$_{12}$)	b.p. 168°/15[26]
1p′		Cl	**3p**	A/ClCH$_2$CH$_2$Cl/14h	90		
1q		Br	**3q**	A/ClCH$_2$CH$_2$Cl$_2$/6h	95	125° (c-C$_6$H$_{12}$/C$_6$H$_6$)	125°[24]
1r		Br	**3r**	A/ClCH$_2$CH$_2$Cl$_2$/24h	90	98° (C$_6$H$_{14}$)	88°[27]
				B^h/CH$_3$CN/20h	95		
1r′		Cl	**3r**	A/ClCH$_2$CH$_2$Cl/24h	90		
1r″		OH	**3r**	C/C$_6$H$_6$/4.5h	98		
1s		Br	**3s**	A/ClCH$_2$CH$_2$Cl/30h	99	110° (c-C$_6$H$_{12}$)	110°[24]
				B^b/CH$_3$CN/29h	94		
				B^f/CH$_3$CN/29h	98		
				B^g/CH$_3$CN/48h	94		
1t		Br, Br	**3t**	A^i/ClCH$_2$CH$_2$Cl/4h	95	124° (c-C$_6$H$_{12}$)	124°[28]
1t″		OH, OH	**3t**	C/C$_6$H$_6$/10h	93		
1u		Br, Br	**3u**	A^i/ClCH$_2$CH$_2$Cl/5h	96	139° (c-C$_6$H$_{12}$)	C$_8$H$_7$NO$_3$ (163.1)
1v		Br	**3v**	A/ClCH$_2$CH$_2$Cl/2h	83	157° [(i-C$_3$H$_7$)$_2$O/ C$_2$H$_5$OAc]	C$_{10}$H$_6$O$_3$ (178.3)
1w		Br	**3w**	A/ClCH$_2$CH$_2$Cl/3h	87	138° [(i-C$_3$H$_7$)$_2$O/ C$_2$H$_5$OAc]	131–132°[29]
1x		Br	**3x**	A/ClCH$_2$CH$_2$Cl/3h	58	182° (C$_2$H$_5$OAc)	178°[30]
1y		Br, Br	**3y**	B/CH$_3$CN/2h	92	133° (c-C$_6$H$_{12}$/C$_6$H$_6$)	131–132°[31]
1y″		OH, OH	**3y**	C/C$_6$H$_6$/10h	95		
1z		Br, Br	**3z**	B^f/CH$_3$CN/30h	97	149° (c-C$_6$H$_{12}$/C$_6$H$_6$)	149°[23]
				B^h/CH$_3$CN/24h	95		
1aa		Br	**3aa**	B^f/CH$_3$CN/20h	75	118° (c-C$_6$H$_{12}$)	118°[23]
1bb″		Cl, Cl	**3bb**	B/dioxan/5h	91	183° (i-C$_8$H$_{16}$/ C$_6$H$_5$CH$_3$)	C$_{10}$H$_8$Br$_2$O$_4$ (352.0)
1cc		Br, Br	**3cc**	B/CH$_3$CN/16h	95	220° (C$_6$H$_5$CH$_3$)	207°[32]
1dd″		Cl, Cl	**3dd**	B/CH$_3$CN/3h	95	66° (C$_6$H$_{14}$)	68–69°[33]
1ee″		OH	**3ee**	C/C$_6$H$_6$/3h	92	oil	C$_{14}$H$_{18}$O$_7$ (298.3)

Table 1. (continued)

Substrate No.	Ar (or R)	X	Product	Method/solvent/ Reaction Time	Yield [%]	m.p. [°C] (solvent) or b.p. [°C]/torr	Molecular formula[a] or Lit. Data
1 ff″		OH, OH	**3 ff** 	C/C_6H_6/6h	94	182° (C_6H_6/ C_2H_5OAc)	185°[34]
1 gg″		OH	**3 gg**	C/C_6H_6/2h	98	64° (C_6H_{14})	63–64°[35,36]
1 hh″		OH	**3 hh**	C/C_6H_6/2.5h	97	oil	$C_{11}H_{14}O_3$ (194.2)
1 ii″		OH, OH	**3 ii**	C/C_6H_6/2h	92	132° (c-C_6H_{12}/C_6H_6)	129–130°[37]
1 jj″		OH, OH	**3 jj**	C/CH_2Cl_2/17h	63	132° (c-C_6H_{12})	$C_9H_8O_4$ (180.2)
1 kk″		OH, OH	**3 kk**	C/C_6H_6/3h	85	81° (C_6H_{14})	$C_{10}H_{10}O_3$ (178.2)
1 ll″		OH	**3 ll**	C/C_6H_6/4h	93	112° (c-C_6H_{12})	$C_{16}H_{16}O_5$ (188.3)
1 mm″		OH	**3 mm**	C/C_6H_6/9h	98	93° (c-C_6H_{12})	93°[23]
6a		–	**7 a**	C/CH_2Cl_2/7h	100	252–254°/760	253°/760[17]
6b	n-$C_{11}H_{23}$	–	**7 b**	C/C_6H_6/8h	80	42° (C_6H_{14})	44.5°[17]
6c	n-$C_{13}H_{27}$	–	**7 c**	C/C_6H_6/6h	75	25° (C_6H_{14})	30°[17]
6d		–	**7 d** 	C/C_6H_6/9h	97	53° (C_6H_{14})	43–48°[38]

[a] Satisfactory microanalyses obtained: C ±0.4, H ±0.3, Br ±0.4, N ±0.3.
[b] Tetra-*n*-butylammonium bromide added as catalyst.
[c] DME = 1,2-dimethoxyethane. $CH_3OCH_2CH_2OCH_3$
[d] Tetra-*n*-butylammonium chloride added as catalyst.
[e] Terephthalaldehyde isolated as minor (20%) product.
[f] 18-Dibenzocrown-6 ether added as catalyst.
[g] Reaction in acetonitrile/hexamethylphosphoric triamide (9/1, 100 ml).
[h] 18-Crown-6 ether added as catalyst.
[i] Potassium hydrogen phosphate not present.

Benzyl, allylic, and aliphatic alcohols **6** are also oxidized to the corresponding aldehydes with **4** in good yields (Method C, Table 1). The reagent **2** has not been used for this purpose previously, although other similar reagents, e.g. dimethyl sulfoxide (activated with oxalyl chloride, trifluoroacetic anhydride, *N,N'*-dicyclohexylcarbodiimide)[4], bis[*p*-methoxyphenyl] telluroxide[13], benzeneselenic anhydride[14,15], butyl hydroperoxide with dimesityl diselenide were used recently[16]. Our procedure is manipulatively simple and is carried out in benzene under reflux with continuous removal of water formed by molecular sieves placed in the condenser.



$$R-CH_2-OH + O{=}Se(CH_3)_2 \xrightarrow{\text{benzene}, \nabla} R-CH{=}O + H_3C-Se-CH_3 + H_2O$$

6 **2** **7**

In conclusion we have proposed a useful method for the synthesis of polysubstituted aromatic aldehydes bearing substituents reactive toward acids, bases or water, as well as for the synthesis of dialdehydes. Bromomethylene compounds can be oxidized selectively to aldehydes in the presence of a chloromethyl group (**1e** → **3e** in Table 1). The reagent **2** has shown its merit also in the oxidation of non-active hydroxymethyl groups in aliphalic alcohols to aldehydes (Table 1).

Table 2. Spectroscopic Data of Selected Polysubstituted Aromatic and Heteroaromatic Aldehydes

Product	I.R. (KBr) $\nu_{C=O}$ [cm^{-1}]	^1H-N.M.R. ($CDCl_3$/HMDSO)[a] δ [ppm]
3d	1680 (aldehyde) 1730 (ester)	4.14 (s, 3H, OCH_3); 6.83 (d, 1H, $J = 16$ Hz, $=CH-Ar$); 7.92–8.22 (m, 5H, H_{arom} + $=CH-CO-$); 10.34 (s, 1H, CHO)
3g	1690 (aldehyde) 1748 (ester)	2.55 (s, 6H, CH_3); 2.68 (s, 3H, $COCH_3$); 7.90 (s, 2H, H_{arom}) 10.22 (s, 1H, CHO)
3p	1670	3.04 (s, 3H, CH_3); 7.50–8.20 (m, 5H, H_{arom}); 9.22 (dd, 1H, $J = 8$ Hz, $J = 2$ Hz, 8-H); 10.20 (s, 1H, CHO)
3u	1709	4.31 (s, 3H, OCH_3); 7.95 (s, 2H, H_{arom}); 10.43 (s, 1H, CHO)
3v	1703 (aldehyde) 1734 (lactone)	7.26 (s, 1H, $=CH$); 7.72 (m, 3H, H_{arom}); 8.88–9.00 (m, 1H, H_{arom}); 10.48 (s, 1H, CHO)
3bb	1690	4.32 (s, 6H, OCH_3); 10.64 (s, 2H, CHO)
3ee	1700[b]	4.19, 4.21, 4.27, 4.30 (4s, 3H each, OCH_3); 4.18–4.39 (m, 4H, $-CH_2-$); 6.31 (s, 1H, $=CH$); 10.65 (s, 1H, CHO)
3hh	1632[b]	1.47 (d, 6H, $J = 6.5$ Hz, CH_3); 2.78 (s, 3H, $ArCH_3$); 3.66 (quin., 1H, $J = 6.5$ Hz, $=CH$); 6.87 (d, 1H, $J = 7$ Hz, H_{arom}); 7.54 (d, 1H, $J = 7$ Hz, H_{arom})
3jj	1675	4.20 (s, 3H, OCH_3); 7.80 (s, 2H, H_{arom}); 10.50 (s, 2H, CHO) 11.44 (s, 2H, OH)
3kk	1645	1.55 (t, 3H, $J = 7.5$ Hz, CH_3); 3.06 (q, 2H, $J = 7.5$ Hz, $-CH_2-$); 8.22 (d, 1H, $J = 2$ Hz, H_{arom}); 8.28 (d, 1H, $J = 2$ Hz, H_{arom}); 10.22, 10.30 (2s, 1H each, CHO); 12.16 (s, 1H, OH)
3ll	1695	4.35 (s, 6H, OCH_3); 4.30–4.56 (m, 4H, $-CH_2-$); 6.71 (m, 1H, $=CH$); 7.86–7.97 (m, 2H, H_{arom}); 8.40–8.56 (m, 2H, H_{arom})

[a] 100 MHz.

[b] Neat.

Dimethyl Selenoxide (2):

To a vigorously stirred solution of hydrogen peroxide (30%, 40 ml), cooled in an ice-salt bath, dimethyl selenide (32.5 g, 0.34 mol) is added dropwise during 2 h and the mixture is stirred for an additional 30 min. Then platinum/asbestos (20%, 200 mg) is added and the mixture is gently stirred for 17 h at room temperature. After this time, the reaction mixture is filtered and the water is removed in vacuo at below 40 °C. To the liquid residue, chloroform (100 ml) and anhydrous potassium carbonate (60 g) are added and it is allowed to stand overnight. Potassium carbonate is filtered off, washed with chloroform (100 ml) and the chloroform is evaporated in vacuo. The crystalline residue is dissolved in chloroform (100 ml) and dried again with potassium carbonate (40 g). After the removal of potassium carbonate and chloroform, the crystalline residue is dried over phosphorus pentoxide in vacuo, (initially 15 torr, then 0.1 torr). The crude product is recrystallized from dry benzene (70 ml) and dried again in vacuo over phosphorus pentoxide to give pure, anhydrous product; yield: 32.9 g, (91%); m.p. 93 °C (in sealed capillary) (Lit.[39], m.p. 91–93 °C).

Potasssium Benzeneselenite (4)

Benzeneselenic Acid: To an ice-cooled solution of diphenyl diselenide (5; 31 g, 100 mmol) in dichloromethane (200 ml), hydrogen peroxide (30%, 34 ml) is added dropwise with vigorous stirring during 3–4 h and the mixture is stirred for 30 min more. The cold mixture is filtered, the solid washed with cold water (30 ml) and cold dichloromethane (50 ml). Benzeneselenic acid thus obtained is dried in air; yield: 35 g (92%); m.p. 126 °C (Lit.[40], m.p. 124–125 °C).

Conversion of Benzeneselenic Acid to **4**: To a solution of potassium ethoxide prepared from potassium (13.0 g, 0.34 mol) and absolute ethanol (200 ml), benzeneselenic acid (64.3 g, 0.34 mol) is added portionswise. The solution is evaporated in vacuo and the residue is treated with ether (200 ml). The potassium benzeneselenite (**4**) is filtered off, washed with ether and dried in vacuo,; yield: 75 g (97%).

Oxidation of Halomethylarenes 1 to Aromatic Aldehydes 3; General Procedures:

Method A, *Using Dimethyl Selenoxide* (**2**): A solution of halomethylarene **1** (3.0 mmol), dimethyl selenoxide (**2**; 1.0 g, 8.6 mmol) in the appropriate solvent (15 ml, Table 1) and potassium hydrogen phosphate (2.5 g, 15 mmol) are refluxed with vigorous stirring for suitable time (Table 1). When dialdehydes are synthesized, twice the amount of dimethyl selenoxide (**2**) and potassium hydrogen phosphate are used. After cooling, water (50 ml) is added and the layers are separated. The organic layer is dried with magnesium sulfate and the solvent removed in vacuo. The residue is purified by column chromatography on silica gel using chloroform/ethyl acetate (9:1) as eluent.

When acetonitrile is used as a solvent, the reaction mixture is diluted with water, the solid filtered off, and the filtrate purified as described above.

Method B, *Using Potassium Benzeneselenite* (**4**): The appropriate halomethylarene **1** (30 mmol), potassium benzeneselenite (**4**; 6.9 g, 30 mmol) and potassium hydrogen phosphate (5.0 g, 29 mmol) in acetonitrile (90 ml) are refluxed with vigorous stirring for a suitable time (Table 1). When dialdehydes are synthesized, double the amount of potassium benzeneselenite and potassium hydrogen phosphate are used. After cooling, the mixture is diluted with water (200 ml) and extracted with dichloromethane (3 × 50 ml). The extract is dried with sodium sulfate, the solvent is evaporated and the residue is separated on a silica gel (0.063–0.2 mm) column (3 × 20 cm) Diphenyl diselenide (**5**) formed is eluted with petroleum ether (40–60 °C) and recrystallized from ethanol; yield: 3.1 g (76%); m.p. 63 °C (Lit.[41], m.p. 63 °C). After removing diphenyl diselenide, the aldehyde is eluted out with chloroform and then recrystallized from a suitable solvent (Table 1). Aldehydes **3ee** and **3ll** are purified on basic alumina column using hexane/ethyl acetate (4:1) as eluent before recrystallization. In the case of compounds **3bb** and **3cc**, chromatography is omitted and the crude products are recrystallized from suitable solvents.

Oxidation of Aromatic Benzyl Alcohols, Allylic- and Aliphatic Alcohols with Dimethylselenoxide to Aldehydes 7; General Procedure:

Method C: A solution of the appropriate alcohol **6** (2.0 mmol) and dimethyl selenoxide (**2**; 0.5 g, 4.3 mmol) in benzene (10 ml) is refluxed using a condenser in which molecular sieves (3 Å, 3 g, Serva) are placed with aid of glass wool, for a suitable time (Table 1). In the cases where dialdehydes are prepared, double the amount of oxidant is used. After cooling, the mixture is washed with water and dried with sodium sulfate. The solvent is evaporated in vacuo and the residue is purified in the same way as described for Method A.

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