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A Simple and Efficient Conversion of Aldehyde Acetals into Esters[1]

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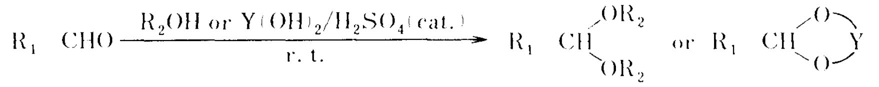
The reaction of aldehydic acetals with hypochlorous acid in acetic acid–acetone afforded the corresponding esters in excellent yields. From cyclic acetals, only the corresponding hydroxyalkyl esters were obtained.

Keywords——acetal; hypochlorite; hypochlorous acid; conversion; ester; hydroxyalkyl ester; regioselectivity

The direct conversion of aldehydic acetals into the corresponding esters could be a useful process in synthetic chemistry. Although this conversion has usually been achieved by oxidation with peracid,[2] ozone[3] or *N*-bromosuccinimide,[4] and by photochemical oxidation,[5] these procedures are not satisfactory in various respects (ease of handling and suitability for large-scale synthesis). In order to develop a versatile procedure for the conversion, the utility of hypochlorous acid was investigated and this acid was found to be a good tool for the oxidation of aldehydic acetals to the corresponding esters.[6] Hypochlorous acid used in this reaction was formed *in situ* from sodium hypochlorite or calcium hypochlorite in acetic acid–acetone. The reactions proceeded readily and cleanly, and could be suitable for providing the oxidized products on an industrial scale.

Results and Discussion

The acetals (**2** and **3**) used were synthesized by the reaction of aldehydes (**1**) with alcohols (methanol, ethanol and glycols) in the presence of a catalytic amount of sulfuric acid, and purified by distillation or silica-gel column chromatography (Chart 1). The yields, boiling



1 **2** **3**

Compd 2	R_1	R_2	Compd 3	R_1	Y
2a	Ph	Et	**3a**	$PhCH_2$	$-CH(CH_3)CH_2-$
2b	$PhCH_2$	Et	**3b**	$PhCH(CH_3)$	$-CH_2CH_2-$
2c	$PhCH_2CH_2$	Et	**3c**	$PhCH(CH_3)$	$-CH_2CH_2CH_2-$
2d	$PhCH(CH_3)$	Me	**3d**	$PhCH(CH_3)$	$-CH(CH_3)CH(CH_3)-$
2e	$PhCH(CH_3)$	Et			
2f	*m*-$BrC_6H_4CH(CH_3)$	Me			
2g	$CH_3CH_2CH_2CH(CH_3)$	Et			

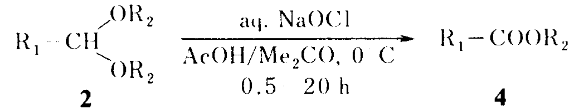
Chart 1

points and proton nuclear magnetic resonance (^{1}H-NMR) chemical shifts of the acetalic proton are shown in Table I.

TABLE I. Yields, Boiling Points and Acetal ^{1}H-NMR Patterns of the Acetals **2** and **3**

Acetal (**2**, **3**)	Yield[a] (%)	bp, °C (mmHg)	^{1}H-NMR chemical shift δ ppm in $CDCl_3$
			Acetal C$\underline{H}$
2a	88.6	77.0—78.0 (5.0)[b]	5.49, s
2b	87.7	91.0—92.0 (8.0)[c]	4.58, t, $J=5.5$ Hz
2c	87.5	103.0—104.0 (2.7)[d]	4.49, t, $J=6.0$ Hz
2d	89.9	82.0—83.2 (3.2)[e]	4.33, d, $J=6.5$ Hz
2e	90.7	92.0—93.0 (3.0)[f]	4.47, d, $J=6.5$ Hz
2f	83.0	114.0—115.0 (2.8)	4.29, d, $J=6.5$ Hz
2g	75.6	75.0—76.0 (19)[g]	4.15, d, $J=6.0$ Hz
3a	86.2	98.0—99.0 (2.8)	4.93—5.23, m
3b	81.4	95.0—96.0 (2.5)[h]	4.87, d, $J=4.5$ Hz
3c	84.4	107.0—108.0 (2.3)	4.53, d, $J=5.0$ Hz
3d	86.4	101.0—102.0 (2.8)	4.94, d, $J=4.0$ Hz 5.16, d, $J=4.0$ Hz

a) Isolated yield by distillation.
b) Reference 2: 75.0 (4 mmHg).
c) Reference 7: 110.0—110.5 °C (12 mmHg).
d) Reference 7: 122.0—123.0 °C (9 mmHg).
e) Reference 8: boiling point was not reported.
f) Reference 9: boiling point was not stated.
g) Reference 10: 67.0 °C (15 mmHg).
h) Reference 11: 93.0—95.0 °C (4 mmHg).



$$R_1-CH(OR_2)_2 \xrightarrow[AcOH/Me_2CO,\ 0\ ^\circ C\ \ 0.5-20\ h]{aq.\ NaOCl} R_1-COOR_2$$

2 **4**

Chart 2

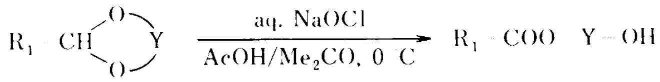
TABLE II. Conversion of Acyclic Acetals (**2**) into Esters (**4**) by Treatment with Hypochlorous Acid

Acetal **2**	Reaction time (h)	Ester **4**		
		Compd **4**	Yield[a] (%)	bp, °C (mmHg)
2a	12	**4a**	85.5	91.0—92.0 (13)[b]
2b	12	**4b**	85.4	91.0—92.0 (10)[c]
2c	5	**4c**	86.1	102.0—103.0 (3.8)[d]
2d	10	**4d**	89.5	78.0—79.0 (3.2)[e]
2e	5	**4e**	90.5	88.0—89.0 (3.8)[f]
2f	20	**4f**	89.5	114.0—116.0 (2.8)
2g	0.5	**4g**	83.7	75.2—76.5 (20)[g]

a) Isolated yield by distillation.
b) Reference 2: 87.0—90.0 °C (10 mmHg).
c) Reference 12: 120.0—125.0 °C (17—18 mmHg).
d) Reference 13: 126.0 °C (15 mmHg).
e) Reference 14: 70.0—71.5 °C (0.5 mmHg).
f) Reference 15: 107.0—110.0 °C (13 mmHg).
g) Reference 16: 153.5—154.0 °C (758 mmHg).

A typical procedure for the oxidation of acetals (**2** and **3**) is as follows. An acyclic acetal (**2**: 1 eq mol) was added to a mixture of acetic acid and acetone under ice-cooling, then *ca.* 13% sodium hypochlorite solution (5 eq mol) was added dropwise to the mixture, and the whole was stirred for 0.5—20 h. After evaporation of the solvent *in vacuo*, the corresponding ester (**4**) was generally obtained in nearly quantitative yield by the usual work-up (Chart 2). Various kinds of acyclic acetals (**2**) were subjected to this oxidation, and the results are summarized in Table II.

This oxidation was also undertaken for the cyclic acetals (**3**) by a similar reaction procedure, and it was found that the cyclic acetals (**3**) were converted into the corresponding hydroxyalkyl esters (**5**) in high yields as shown in Chart 3 and Table III.



3 **5**

Compd. 5	R_1	Y
5a1	$PhCH_2$	$-CH_2CH(CH_3)-$
5a2	$PhCH_2$	$-CH(CH_3)CH_2-$
5b	$PhCH(CH_3)$	$-CH_2CH_2-$
5c	$PhCH(CH_3)$	$-CH_2CH_2CH_2-$
5d	$PhCH(CH_3)$	$-CH(CH_3)CH(CH_3)-$

Chart 3

TABLE III. Conversion of Cyclic Acetals (**3**) into Hydroxyalkyl Esters (**5**) by Treatment with Hypochlorous Acid

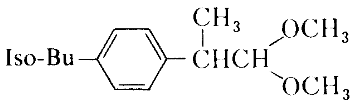
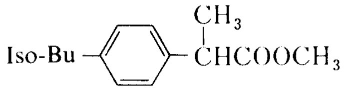
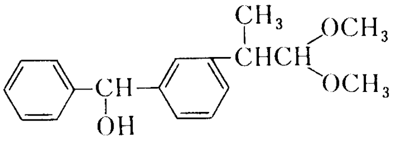
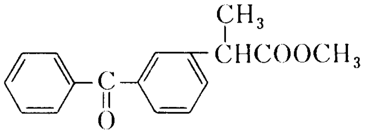
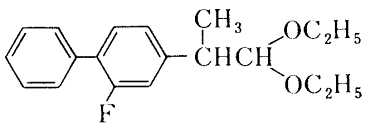
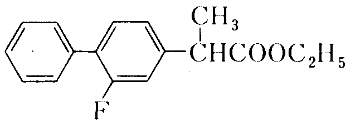
Acetal 3	Reaction time (h)	Ester 5		
		Compd 5	Yield[a] (%)	bp, °C (mmHg)
3a	0.5	**5a**	81.7	136.5—137.7 (3.3)[b,c]
3b	1.0	**5b**	84.7	146.0—147.0 (4.5)
3c	5.0	**5c**	82.4	149.0—150.0 (2.3)
3d	1.0	**5d**	87.1	136.0—137.0 (2.8)

a) Isolated yield by distillation.
b) Boiling point of a 1 : 1 mixture of 2-hydroxypropyl and 1-hydroxy-2-propyl esters.
c) Reference 17: 105.0—107.0 °C (0.5 mmHg).

Prugh *et al.*[18] reported that the oxidation of unsymmetric cyclic acetals with *N*-bromosuccinimide in the presence of azobisisobutyronitrile afforded the corresponding bromoalkyl esters with regioselective acetal ring opening. For example, benzaldehyde propylene acetal yielded 1-bromo-2-propyl and 2-bromopropyl benzoate in a ratio of 5 : 1. In contrast to their results, in our system the unsymmetric cyclic acetal (**3a**) yielded 2-hydroxypropyl (**5a1**) and 1-hydroxy-2-propyl phenylacetate (**5a2**) in a ratio of approximately 1 : 1. From this result, it seems that this oxidation using hypochlorous acid does not proceed regioselectively with unsymmetric cyclic acetals. However, these reactions might be useful for the preparation of monohydroxyalkyl esters from symmetrical cyclic acetals.

In addition, these conversions could also be applied to the preparation of the ester precursors of antiinflammatory drugs of the arylalkanoic acid type. Some examples are shown in Table IV.

Table IV. Application to the Preparation of Commercially Available Drugs

Acetal	Yield[a] (%)	Product	
		Ester	Yield[c] (%)
	84.7		87.2[d]
	79.6[b]		88.6[e,f]
	83.7		86.3[g]

a) Isolated yield by distillation unless otherwise noted.
b) Isolated by silica-gel column chromatography.
c) Isolated yield by silica-gel column chromatography.
d) Reference 19: bp 109—110 C (1.8 mmHg).
e) The benzylic OH group is also oxidized under the present conditions to afford the corresponding ketone.
f) Reference 20.
g) Reference 21.

In order to clarify the reaction mechanism and to optimize the reaction conditions, various reaction conditions were examined. When the reaction was carried out in a mixed solvent of acetone–dilute hydrochloric or sulfuric acid, the hydrolysis of acetals occurred predominantly and subsequent oxidation afforded the corresponding carboxylic acids along with trace amounts of esters. On the other hand, when the reaction was carried out in acetone medium, which was alkaline, the conversion was not observed and the starting acetals were recovered almost completely. Consequently, it was concluded that suitable acidic conditions are necessary for this reaction, and the addition of acetic acid was found to be effective for promoting the reaction. The acetals (**2** and **3**) were found to be stable even under such acidic conditions and the oxidation proceeded without hydrolysis. Furthermore, it was found that the reaction of acetophenone ethylene acetal with hypochlorous acid did not occur under the present conditions.

Although it is difficult to clarify the nature of the true reacting species, it is considered that Cl^+ (or Cl_2) formed from hypochlorous acid in acidic medium might be involved as an active reacting species.[22] Consequently, a plausible mechanism could be as shown in Chart 4.

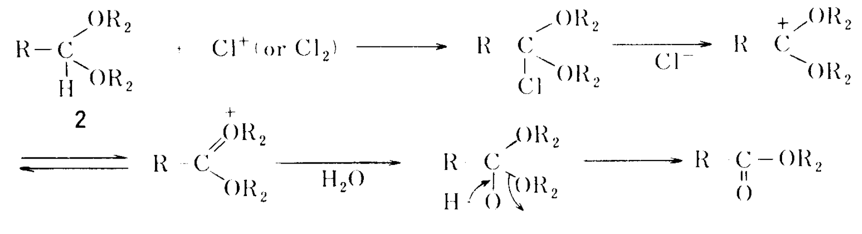


Chart 4

In conclusion, this method permits the conversion of aldehyde acetals into the corresponding esters by a simple and straight forward oxidation using sodium hypochlorite. It could be applicable to the preparation of esters on a manufacturing scale.

Experimental

All boiling points are uncorrected. Infrared (IR) spectra were taken with JASCO IRA-I spectrophotometer and mass spectra (MS) were recorded on a Hitachi RM-50 spectrometer with 30 eV ionization energy. ^{1}H-NMR spectra were obtained on a Hitachi R-24 (60 MHz) spectrometer using tetramethylsilane as an internal standard and chemical shifts are shown in δ ppm. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Starting Materials——All the acetals except for **2a** used in this work were synthesized by acetalization of the aldehydes (**1**) with alcohols. Compound **2a** was prepared by the reaction of benzaldehyde with ethyl orthoformate.

Benzaldehyde Diethyl Acetal (2a)——Ethyl orthoformate (18.1 g, 122 mmol) and ammonium nitrate (500 mg) were added to benzaldehyde (11.3 g, 106 mmol) and the reaction mixture was stirred for 1.5 h at 50 °C, then cooled. Benzene (50 ml) was added to the reaction mixture and the solution was washed successively with 10% $\mathrm{Na_2CO_3}$ solution (20 ml) and water (10 ml × 2), and dried over anhydrous sodium sulfate. Evaporation of the benzene followed by distillation of the residual product gave **2a** as a colorless oil. See also Table I and ref. 2.

General Procedure for the Preparation of the Acetals (2b—j, 3a—d)——Conc. $\mathrm{H_2SO_4}$ (300 mg) was added to a solution of an aldehyde (30 mmol) in EtOH (18 ml) and the reaction mixture was stirred for 15 min at room temperature. The title acetal was then obtained as a colorless oil according to the procedure described for **2a**.

Phenylacetaldehyde Diethyl Acetal (2b)——^{1}H-NMR ($\mathrm{CDCl_3}$) δ ppm: 1.15 (6H, t, $J=7$ Hz, $\mathrm{CH_3\times 2}$), 2.85 (2H, d, $J=5.5$ Hz, $\mathrm{C\underline{H}_2Ph}$), 3.47 (2H, q, $J=7$ Hz, $\mathrm{C\underline{H}_2CH_3}$), 3.60 (2H, q, $J=7$ Hz, $\mathrm{C\underline{H}_2CH_3}$), 4.58 (1H, t, $J=5.5$ Hz, CH), 7.20 (5H, s, Ph). MS *m/z*: 149 ($\mathrm{M^+-OEt}$), 148, 120, 105, 92, 91 (base peak), 77.

3-Phenylpropanal Diethyl Acetal (2c)——^{1}H-NMR ($\mathrm{CDCl_3}$) δ ppm: 1.21 (6H, t, $J=7$ Hz, $\mathrm{CH_3\times 2}$), 1.81—2.07 (2H, m, $\mathrm{PhCH_2C\underline{H}_2}$), 2.59—2.83 (2H, m, $\mathrm{PhC\underline{H}_2}$), 3.28—3.75 (4H, m, $\mathrm{OC\underline{H}_2CH_3\times 2}$), 4.49 (1H, t, $J=6$ Hz, CH), 7.18 (5H, s, Ph). MS *m/z*: 163 ($\mathrm{M^+-OEt}$), 162, 133, 118, 117, 115, 105 (base peak), 103, 92, 91, 79, 77.

2-Phenylpropanal Dimethyl Acetal (2d)——^{1}H-NMR ($\mathrm{CDCl_3}$) δ ppm: 1.25 (3H, d, $J=6.5$ Hz, $\mathrm{CHC\underline{H}_3}$), 2.89 (1H, quintet, $J=6.5$ Hz, $\mathrm{C\underline{H}CH_3}$), 3.20 (3H, s, $\mathrm{OCH_3}$), 3.33 (3H, s, $\mathrm{OCH_3}$), 4.33 (1H, d, $J=6.5$ Hz, $\mathrm{CH{<}^{O}_{O}}$), 7.20 (5H, s, Ph). MS *m/z*: 149 ($\mathrm{M^+-OMe}$), 148, 133, 117, 115, 105 (base peak), 103, 91, 79, 77.

2-Phenylpropanal Diethyl Acetal (2e)——^{1}H-NMR ($\mathrm{CDCl_3}$) δ ppm: 1.01 (3H, t, $J=7$ Hz, $\mathrm{CH_2C\underline{H}_3}$), 1.28 (3H, t, $J=7$ Hz, $\mathrm{CH_2C\underline{H}_3}$), 1.32 (3H, d, $J=6.5$ Hz, $\mathrm{CHC\underline{H}_3}$), 2.98 (1H, quintet, $J=6.5$ Hz, $\mathrm{C\underline{H}CH_3}$), 3.52 (4H, m, $\mathrm{OC\underline{H}_2CH_3\times 2}$), 4.47 (1H, d, $J=6.5$ Hz, $\mathrm{CH{<}^{O}_{O}}$), 7.26 (5H, s, Ph). MS *m/z*: 163 ($\mathrm{M^+-OEt}$), 162, 134, 133, 115, 105 (base peak), 103, 91, 79, 77.

2-(3-Bromophenyl)propanal Dimethyl Acetal (2f)——^{1}H-NMR ($\mathrm{CDCl_3}$) δ ppm: 1.23 (3H, d, $J=6.5$ Hz, $\mathrm{CHC\underline{H}_3}$), 2.89 (1H, quintet, $J=6.5$ Hz, $\mathrm{C\underline{H}CH_3}$), 3.19 (3H, s, $\mathrm{OCH_3}$), 3.30 (3H, s, $\mathrm{OCH_3}$), 4.29 (1H, d, $J=6.5$ Hz, $\mathrm{CH{<}^{O}_{O}}$), 7.06—7.45 (4H, m, aromatic). MS *m/z*: 229, 227 ($\mathrm{M^+-OMe}$, 1 : 1), 226, 185, 132, 104, 103, 77, 75 (base peak). *Anal.* Calcd for $\mathrm{C_{11}H_{15}BrO_2}$: C, 50.98; H, 5.83. Found: C, 51.10; H, 5.59. The starting aldehyde used in this reaction was prepared from 2-(3-bromophenyl)-2-methyloxirane with synthetic aluminium silicate, and the oxirane was synthesized from 3-bromoacetophenone with trimethylsulfonium methylsulfate in the presence of sodium methoxide.[23] Their physical properties and spectral data were as follows.

2-(3-Bromophenyl)-2-methyloxirane: A colorless oil. $\mathrm{bp_{1.0}}$ 74.0—76.0 °C. ^{1}H-NMR ($\mathrm{CDCl_3}$) δ ppm: 1.65 (3H, s, $\mathrm{CH_3}$), 2.70, 2.92 (2H, ABq, $J=6$ Hz, $\mathrm{CH_2}$), 7.00—7.50 (4H, m, aromatic). MS *m/z*: 214, 212 ($\mathrm{M^+}$, 1 : 1), 199, 197, 155, 152.

2-(3-Bromophenyl)propanal: A colorless oil. $\mathrm{bp_{1.0}}$ 87.0—90.0 °C. IR $\nu_{\mathrm{max}}^{\mathrm{film}}\,\mathrm{cm^{-1}}$: 1715 (C=O). ^{1}H-NMR ($\mathrm{CDCl_3}$) δ ppm: 1.38 (3H, d, $J=7$ Hz, $\mathrm{CH_3}$), 3.54 (1H, qd, $J=7$, 1.5 Hz, $\mathrm{C\underline{H}CH_3}$), 7.00—7.50 (4H, m, aromatic), 9.60 (1H, d, $J=1.5$ Hz, CHO). MS *m/z*: 214, 212 ($\mathrm{M^+}$, 1 : 1), 199, 197.

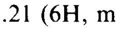
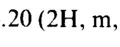
2-Methylpentanal Diethyl Acetal (2g)——^{1}H-NMR ($\mathrm{CDCl_3}$) δ ppm: 0.88 (3H, d, $J=6.5$ Hz, $\mathrm{CHC\underline{H}_3}$), 1.18 (9H, t, $J=7$ Hz, $\mathrm{CH_2CH_2C\underline{H}_3}$ and $\mathrm{OCH_2C\underline{H}_3\times 2}$), 1.20—1.80 (5H, m, $\mathrm{C\underline{H}_2C\underline{H}_2CH_3}$ and $\mathrm{C\underline{H}CH_3}$), 3.55 (2H, q, $J=7$ Hz, $\mathrm{OC\underline{H}_2CH_3}$), 3.64 (2H, q, $J=7$ Hz, $\mathrm{OC\underline{H}_2CH_3}$), 4.15 (1H, d, $J=6$ Hz, $\mathrm{CH{<}^{O}_{O}}$). MS *m/z*: 129 ($\mathrm{M^+-OEt}$), 128, 103, 100, 99, 85, 71 (base peak), 69, 55.

Phenylacetaldehyde Propylene Acetal (3a)——A diastereoisomeric mixture. ^{1}H-NMR ($\mathrm{CDCl_3}$) δ ppm: 1.14 (3H, d, $J=6$ Hz, $\mathrm{CH_3}$), 2.90 (2H, d, $J=5$ Hz, $\mathrm{PhC\underline{H}_2}$), 3.28 (1H, t-like, $\mathrm{O\underset{H}{C}\underline{H}CH(CH_3)O}$), 3.63—4.31 (2H, m, $\mathrm{O\underset{\underline{H}}{C}HC\underline{H}(CH_3)O}$), 4.93—5.23 (1H, m, $\mathrm{CH{<}^{O}_{O}}$), 7.25 (5H, s, Ph). MS *m/z*: 178 ($\mathrm{M^+}$), 177, 133, 119, 105, 104, 103, 92, 91, 87 (base peak), 77, 65. *Anal.* Calcd for $\mathrm{C_{11}H_{14}O_2}$: C, 74.13; H, 7.92. Found: C, 74.34; H, 7.70.

2-Phenylpropanal Ethylene Acetal (3b)——^{1}H-NMR ($\mathrm{CDCl_3}$) δ ppm: 1.27 (3H, d, $J=6.5$ Hz, $\mathrm{CH_3}$), 2.86 (1H, qd, $J=6.5$, 4.5 Hz, $\mathrm{C\underline{H}CH_3}$), 3.72 (4H, s, $\mathrm{OCH_2CH_2O}$), 4.87 (1H, d, $J=4.5$ Hz, $\mathrm{CH{<}^{O}_{O}}$), 7.25 (5H, s, Ph). MS *m/z*: 178

(M^+), 177, 176, 132, 117, 115, 105, 103, 91, 79, 77, 73 (base peak).

2-Phenylpropanal Trimethylene Acetal (3c)——^{1}H-NMR ($CDCl_3$) δ ppm: 1.26 (3H, d, $J=7$ Hz, CH_3), 1.52—2.34 (2H, m, $OCH_2C\underline{H}_2CH_2O$), 2.90 (1H, qd, $J=7$, 5 Hz, $C\underline{H}CH_3$), 3.38—4.16 (4H, m, $OC\underline{H}_2CH_2C\underline{H}_2O$), 4.53 (1H, d, $J=5$ Hz, $CH{<}^{O}_{O}$), 7.21 (5H, s, Ph). MS m/z: 192 (M^+), 191, 161, 132, 117, 106, 105, 103, 91, 88, 87 (base peak), 79, 77. *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97: H, 8.39. Found: C, 74.83; H, 8.30.

2-Phenylpropanal 1,2-Dimethylethylene Acetal (3d)——A diastereoisomeric mixture. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.97—1.21 (6H, m, ), 1.34 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 2.95 (1H, qd, $J=7$, 4 Hz, $C\underline{H}CH_3$), 3.24—3.63, 3.92—4.20 (2H, m, ), 4.94 (0.5H, d, $J=4$ Hz, $CH{<}^{O}_{O} \times 1/2$), 5.16 (0.5H, d, $J=4$ Hz, $CH{<}^{O}_{O} \times 1/2$), 7.30 (5H, s, Ph). MS m/z: 206 (M^+), 205, 147, 133, 118, 117, 105, 103, 102, 101 (base peak), 91, 89, 87, 83, 77. *Anal.* Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.70; H, 8.66.

2-(4-Isobutylphenyl)propanal Dimethyl Acetal——A colorless oil. $bp_{3.2}$ 115.2—116.4 °C. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.89 (6H, d, $J=7$ Hz, $CH(C\underline{H}_3)_2$), 1.23 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 1.54—2.13 (1H, m, $C\underline{H}(CH_3)_2$), 2.44 (2H, d, $J=7$ Hz, $C\underline{H}_2C_6H_4$), 3.01 (1H, quintet, $J=7$ Hz, $C\underline{H}CH_3$), 3.23 (6H, s, $OCH_3 \times 2$), 4.27 (1H, d, $J=7$ Hz, $CH{<}^{O}_{O}$), 7.20 (4H, s, aromatic). MS m/z: 205 ($M^+ - OMe$), 204, 188, 176, 162, 161 (base peak), 146, 145, 131, 118, 117, 105, 91, 75. *Anal.* Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 76.24; H, 9.96.

2-(3-(α-Hydroxybenzyl)phenyl)propanal Dimethyl Acetal——Obtained as a colorless oil after purification by silica-gel column chromatography. ^{1}H-NMR ($CDCl_3$) δ ppm: 1.20 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 2.88 (1H, q, $J=7$ Hz, $C\underline{H}CH_3$), 3.15 (6H, s, $OCH_3 \times 2$), 3.48 (1H, br s, OH disappeared with D_2O), 4.36 (1H, d, $J=7$ Hz, $CH{<}^{O}_{O}$), 5.68 (1H, s, $PhC\underline{H}OH$), 7.15—7.40 (9H, m, aromatic). MS m/z: 269 ($M^+ - OH$), 268, 254, 252, 238, 209, 175, 128, 114, 105 (base peak), 91, 77. *Anal.* Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.75. Found: C, 75.33; H, 7.94.

2-(2-Fluorobiphenyl-4-yl)propanal Diethyl Acetal——A colorless oil. $bp_{2.0}$ 169.0—171.0 °C. ^{1}H-NMR ($CDCl_3$) δ ppm: 1.07 (3H, t, $J=7$ Hz, $OCH_2C\underline{H}_3$), 1.19 (3H, t, $J=7$ Hz, $OCH_2C\underline{H}_3$), 1.32 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 2.98 (1H, m, $C\underline{H}CH_3$), 3.51 (4H, q, $J=7$ Hz, $C\underline{H}_2CH_3 \times 2$), 4.43 (1H, d, $J=6.5$ Hz, $CH{<}^{O}_{O}$), 6.78—7.68 (8H, m, aromatic). MS m/z: 257 ($M^+ - OEt$), 256, 228, 227, 199 (base peak), 185, 103, 77, 74. *Anal.* Calcd for $C_{19}H_{23}FO_2$: C, 75.47; H, 7.67. Found: C, 75.24; H, 7.75.

General Procedure for the Conversion of Acetals into Esters with Hypochlorous Acid——An acetal (20 mmol) was added to a mixed solvent of acetic acid (10 ml) and acetone (50 ml) in an ice bath, then *ca.* 13% aqueous sodium hypochlorite solution (100 mmol) was added slowly to the mixture with stirring to complete the reaction. The progress of the reaction was monitored by thin-layer chromatography (TLC) on silica gel plates (benzene) or by gas liquid chromatography (GLC) (XE-60). In general, the reaction was complete within 0.5—2.0 h. After completion of the reaction, the solution was concentrated *in vacuo* and the residual mixture was dissolved in benzene (100 ml). The extract was washed successively with water (20 ml), 10% sodium hydroxide solution (15 ml) and brine, and dried over anhydrous sodium sulfate. After evaporation of the benzene, purification of the residue by distillation or silica-gel column chromatography gave the pure ester in good yield (Tables II, III and IV). The structures of the esters obtained were confirmed by the spectral data and physical characteristics. Sodium hypochlorite was used after titrimetrical determination of oxidative power.

Ethyl Benzoate (**4a**): A colorless oil. See Table II and ref. 2.

Ethyl Phenylacetate (**4b**): A colorless oil. See Table II and ref. 12.

Ethyl 3-Phenylpropanoate (**4c**): A colorless oil. See Table II and ref. 13.

Methyl 2-Phenylpropanoate (**4d**): A colorless oil. See Table II and ref. 14.

Ethyl 2-Phenylpropanoate (**4e**): A colorless oil. See Table II and ref. 15.

Methyl 2-(3-Bromophenyl)propanoate (**4f**): A colorless oil. IR ν_{max}^{film} cm^{-1}: 1735 (C=O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.48 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 3.61 (3H, s, OCH_3), 3.75 (1H, q, $J=7$ Hz, $C\underline{H}CH_3$), 7.00—8.00 (4H, m, aromatic). MS m/z: 244, 242 (M^+, 1 : 1), 185, 183, 157, 155, 119, 104, 103, 78, 77. *Anal.* Calcd for $C_{10}H_{11}BrO_2$: C, 49.40; H, 4.56. Found: C, 49.62; H, 4.52.

Ethyl 2-Methylpentanoate (**4g**): A colorless oil. IR ν_{max}^{film} cm^{-1}: 1725 (C=O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.10 (3H, d, $J=6.5$ Hz, $CHC\underline{H}_3$), 1.22 (3H, t, $J=6.5$ Hz, $OCH_2C\underline{H}_3$), 1.15—2.40 (7H, m, $C\underline{H}_3C\underline{H}_2C\underline{H}_2CHCH_3$), 4.06 (2H, q, $J=6.5$ Hz, $OC\underline{H}_2CH_3$). MS m/z: 114 (M^+), 99, 72, 71, 57.

2-Hydroxypropyl Phenylacetate (**5a1**) and 1-Hydroxy-2-propyl Phenylacetate (**5a2**): A colorless oil consisting of nearly equal amounts of **5a1** and **5a2**. The following spectral data were obtained for the mixture. IR ν_{max}^{film} cm^{-1}: 3420 (OH), 1725 (C=O). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.02—1.15 (3H, d-like × 2, CH_3), 3.60 (2H, s, $PhC\underline{H}_2$), 3.65 (1H, d-like, $C\underline{H}_2OH \times 1/2$), 3.95 (1H, d-like, $COOCH_2 \times 1/2$), 3.97 (1H, br s, OH disappeared with D_2O), 4.29 (0.5H, m, $CH_2C\underline{H}OH \times 1/2$), 4.93 (0.5H, m, $OC\underline{H}CH_2OH \times 1/2$), 7.23 (5H, s, Ph). MS m/z: 194 (M^+), 177, 176, 163, 150, 149, 137, 119, 118, 105, 104, 92, 91, 90, 79, 77.

2-Hydroxyethyl 2-Phenylpropanoate (**5b**): A colorless oil. IR$_{\max}^{\text{film}}$cm^{-1}: 3400 (OH), 1720 (C=O). ^{1}H-NMR ($CDCl_3$) δppm: 1.45 (3H, d, J=7 Hz, CH_3), 3.37 (1H, q, J=7 Hz, $C\underline{H}CH_3$), 3.38 (1H, br s, OH disappeared with D_2O), 3.68 (2H, m, $CH_2C\underline{H}_2OH$), 4.04 (2H, m, $OC\underline{H}_2CH_2OH$), 7.26 (5H, s, Ph). MS *m/z*: 194 (M^+), 177, 151, 150, 133, 132, 106, 105, 104, 103, 91, 79, 77. *Anal.* Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.28; H, 6.98.

3-Hydroxypropyl 2-Phenylpropanoate (**5c**): A colorless oil. IR $\nu_{\max}^{\text{film}}$cm^{-1}: 3400 (OH), 1725 (C=O). ^{1}H-NMR ($CDCl_3$) δppm: 1.47 (3H, d, J=7 Hz, CH_3), 1.70 (2H, quintet, J=6 Hz, $CH_2C\underline{H}_2CH_2$), 3.09 (1H, s, OH, disappeared with D_2O), 3.47 (2H, t, J=6 Hz, $C\underline{H}_2OH$), 3.68 (1H, q, J=7 Hz, $CH_3C\underline{H}$), 4.14 (2H, t, J=6 Hz, $COOCH_2$), 7.24 (5H, s, Ph). MS *m/z*: 208 (M^+), 178, 151, 132, 106, 105, 104, 103, 91, 79, 77. *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.20; H, 7.75. Found: C, 69.48; H, 7.48.

3-Hydroxy-2-butyl 2-Phenylpropanoate (**5d**): A colorless oil. IR $\nu_{\max}^{\text{film}}$cm^{-1}: 3400 (OH), 1720 (C=O). ^{1}H-NMR ($CDCl_3$) δppm: 0.96 (3H, d, J=6.5 Hz, $C\underline{H}_3CHOH$), 1.16 (3H, d, J=6.5 Hz, $COOCHC\underline{H}_3$), 1.46 (3H, d, J=7 Hz, $PhCHC\underline{H}_3$), 2.45 (1H, s, OH disappeared with D_2O), 3.72 (1H, q, J=7 Hz, $PhC\underline{H}$), 4.60—5.01 (2H, m, $C\underline{H}(CH_3)C\underline{H}(CH_3)$), 7.28 (5H, s, Ph). MS *m/z*: 204 (M^+), 178, 150, 133, 132, 106, 105, 104, 103, 91, 79, 77. *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.04; H, 7.96.

Methyl 2-(4-Isobutylphenyl)propanoate: A colorless oil. IR $\nu_{\max}^{\text{film}}$cm^{-1}: 1735 (C=O). ^{1}H-NMR ($CDCl_3$) δppm: 0.92 (6H, d, J=6 Hz, $CH(C\underline{H}_3)_2$), 1.45 (3H, d, J=7 Hz, $PhC\underline{H}CH_3$), 1.95 (1H, m, $C\underline{H}(CH_3)_2$), 2.48 (2H, d-like, $C\underline{H}_2C_6H_4$), 3.60 (3H, s, OCH_3), 3.65 (1H, q, J=7 Hz, $PhC\underline{H}$), 7.10—7.90 (4H, m, aromatic). MS *m/z*: 220 (M^+), 177, 176, 162, 161, 145, 121, 119, 118, 105, 91.

Methyl 2-(3-Benzoylphenyl)propanoate: A colorless oil. IR $\nu_{\max}^{\text{film}}$cm^{-1}: 1730 (C=O), 1665 (C=O). ^{1}H-NMR ($CDCl_3$) δppm: 1.50 (3H, d, J=7 Hz, $CHC\underline{H}_3$), 3.62 (3H, s, OCH_3), 3.80 (1H, q, J=7 Hz, $C\underline{H}CH_3$), 7.20—7.85 (9H, m, aromatic). MS *m/z*: 268 (M^+), 224, 210, 209, 191, 181, 165, 105, 77.

Ethyl 2-(2-Fluorobiphenyl-4-yl)propanoate: A colorless oil. IR $\nu_{\max}^{\text{film}}$cm^{-1}: 1730 (C=O). ^{1}H-NMR ($CDCl_3$) δppm: 1.15 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.46 (3H, d, J=7 Hz, $CHC\underline{H}_3$), 3.67 (1H, q, J=7 Hz, $PhC\underline{H}$), 4.14 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.90—7.75 (8H, m, aromatic). MS *m/z*: 272 (M^+) 227, 199, 195, 185, 184, 171, 95, 94, 77.

Alternative Conversion of Acetals into Esters Using Calcium Hypochlorite Reagent: Compound **2i** was converted into the corresponding ester (**4i**) in 89.3% yield by treatment with approximately 50% $Ca(OCl)_2$ in acetic acid and acetone according to the same procedure as described for the use of sodium hypochlorite.

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