

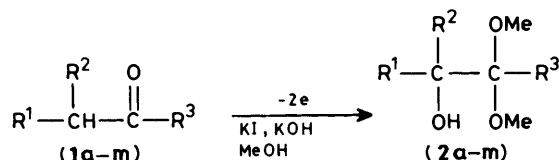
Electro-organic Chemistry. Part 93.† Electro-organic Transformation of Aldehydes and Ketones to α -Hydroxylated Acetals Utilizing Mediators and Some Synthetic Uses of the Products¹

Tatsuya Shono,* Yoshihiro Matsumura, Kenji Inoue, and Fumiaki Iwasaki

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606, Japan

Electro-oxidation of aldehydes (R^1R^2CHCHO) and ketones ($R^1R^2CHCOR^3$) in methanol containing iodide ion (I^-) and KOH gave the corresponding α -hydroxylated acetals [$R^1R^2C(OH)CH(OMe)_2$ and $R^1R^2C(OH)C(OMe)_2R^3$, respectively] in good yields. The first step of this oxidation is explained in terms of the attack of an anodically generated active iodine species ' I^+ ' on enols of R^1R^2CHCHO and $R^1R^2CHCOR^3$. α -Hydroxy acetals were useful starting materials as exemplified by reaction with aniline or methyl carbamates in the presence of Lewis acids to afford β -keto amine derivatives. The anodic oxidation of α -hydroxy acetals was also carried out.

Although a variety of methods have already been exploited for the α -oxygenation of carbonyl compounds (**1**), they are not always useful in practical syntheses, since they generally require enols of (**1**) as the starting materials² and/or more than 1 equiv. of particular oxidizing agents.³



- a $R^1 = (CH_2)_2Me$, $R^2 = R^3 = H$
 b $R^1 = (CH_2)_5Me$, $R^2 = R^3 = H$
 c $R^1 = (CH_2)_7Me$, $R^2 = R^3 = H$
 d $R^1 = CHMe_2$, $R^2 = R^3 = H$
 e $R^1 = R^2 = Et$, $R^3 = H$
 f $R^1 = (CH_2)_3Me$, $R^2 = Et$, $R^3 = H$
 g $R^1, R^2 = (CH_2)_5$, $R^3 = H$
 h $R^1 = CH_2Ph$, $R^2 = R^3 = H$
 i $R^1 = Ph$, $R^2 = Me$, $R^3 = H$
 j $R^1 = (CH_2)_3CO_2Me$, $R^2 = R^3 = H$
 k $R^1, R^3 = (CH_2)_4$, $R^2 = H$
 l $R^1, R^3 = CH_2O(CH_2)_2$, $R^2 = H$
 m $R^1 = (CH_2)_4Me$, $R^2 = H$, $R^3 = Me$

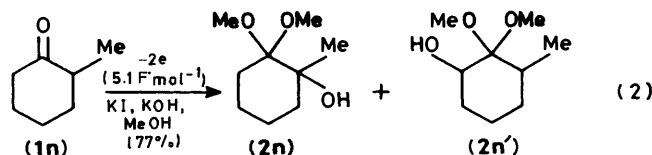
We now report a new method for the direct transformation of (**1**) to α -hydroxylated acetals (**2**), by electro-oxidation, a method which has the advantage that no special oxidizing agent is required [Equation (1)].⁴

Thus, a solution of (**1**) in methanol containing KI and KOH was electrolysed with a constant current and external cooling (ice-water bath) in order to avoid base-catalysed aldol condensation of (**1**); work up of the mixture afforded compound (**2**). That a diaphragm was not required allowed a simple operation and easy work-up. The results are summarized in the Table. Oxidation of unsymmetrical ketone (**1n**) gave a mixture

Table. α -Hydroxylation of carbonyl compounds (**1**) by electro-oxidation^a

Run	Carbonyl compounds (1a-m)	Electricity passed ($F \text{ mol}^{-1}$)	Isolated yield (%) (2a-m)
1	(1a)	3.3	(2a) 62
2	(1b)	4.3	(2b) 75
3	(1c)	4.9	(2c) 85
4	(1d)	2.5	(2d) 62
5	(1e)	5.0	(2e) 67
6	(1f)	5.0	(2f) 78
7	(1g)	4.9	(2g) 76 ^b (78; ^c 78 ^d)
8	(1h)	3.8	(2h) 80
9	(1i)	9.3	(2i) 51 ^e
10	(1j)	5.2	(2j) 33
11	(1k)	5.1	(2k) 74 (64) ^f
12	(1l)	5.7	(2l) 74
13	(1m)	27.4	(2m) 71

^a The electrolysis was carried out under conditions described below: (**1**) (4 mmol), KOH (4 mmol), KI (2 mmol), methanol (30 ml), Pt plate anode, carbon rod cathode. A diaphragm was not used. ^b Methyl cyclohexanecarboxylate (10%) was a by-product. ^c NaI was used instead of KI. ^d Et_4NI was used instead of KI. ^e (**10**) was a by-product (26%). ^f KOH was not used.



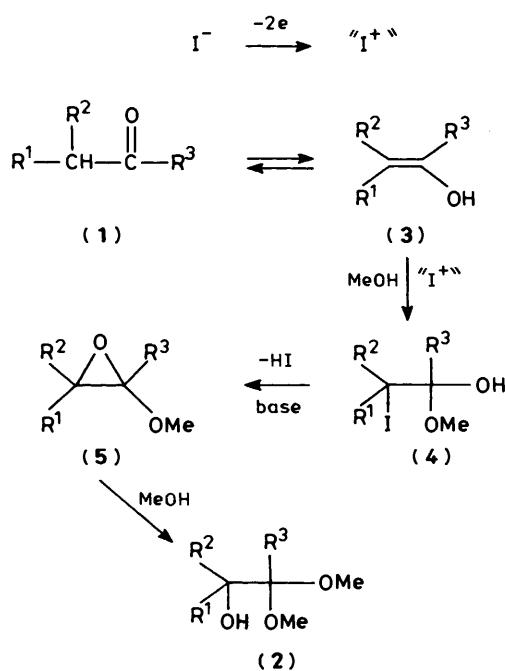
of α - and α' -hydroxylated ketals (**2n**) and (**2n'**) in a ratio of 82:18 [Equation (2)].

The initiation step may involve the oxidation of I^- to a positively charged iodine species ' I^+ ' which then attacks the enols (**3**) to yield the iodohydrins (**4**).[†] The subsequent reaction

[†] A reaction pathway involving I_2 as an oxidizing agent may be conceivable as an alternative mechanism. However, treatment of (**1h**) or (**1i**) (4 mmol) with I_2 (1 equiv.) under basic conditions (30 ml methanol, 1 equiv. KOH) afforded complex products which were certainly different from α -hydroxylated acetals (**2h**) or (**2i**).

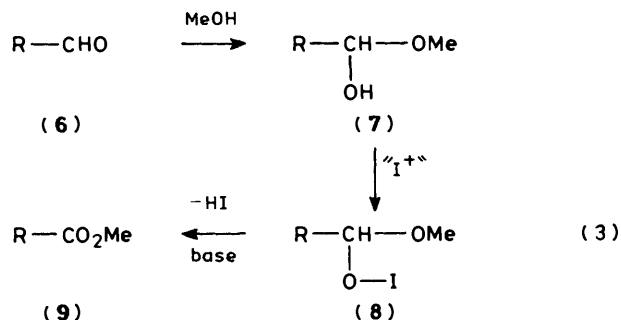
† Part 92, T. Shono, Y. Matsumura, and K. Inoue, *J. Org. Chem.*, in the press.

of (4) with base affords (2) through the intermediate formation of (5) (Scheme 1).



Scheme 1.

Since the reaction medium of electrolysis of (1) was strongly basic, the concentration of the enols (3) may be enough to be attacked by 'I+'. On the other hand, when oxidation of (1) was carried out under neutral conditions, namely without using KOH, aldehydes (6) were oxidised to the esters (9) through the attack of 'I+' on the hemiacetals (7) followed by the elimination of HI by a base as has already been presented [Equation (3)];⁵



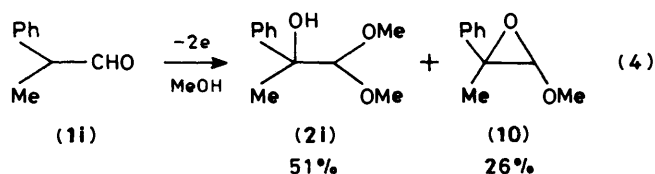
the oxidation of ketones was extremely slow except for the oxidation of cyclohexanone (run 11).*

The postulated Scheme 1 is also supported by the fact that the electro-oxidation of (1i) gave 2-methoxy-3-methyl-3-phenyl-oxirane (10) in 26% yield as a by-product together with the α -hydroxylated acetal (2i) (Equation (4)).[†]

The reaction of (4) with base regenerates iodide ion (I^-) which is reoxidized to 'I+' indicating that iodine ions (I^- , I^+)

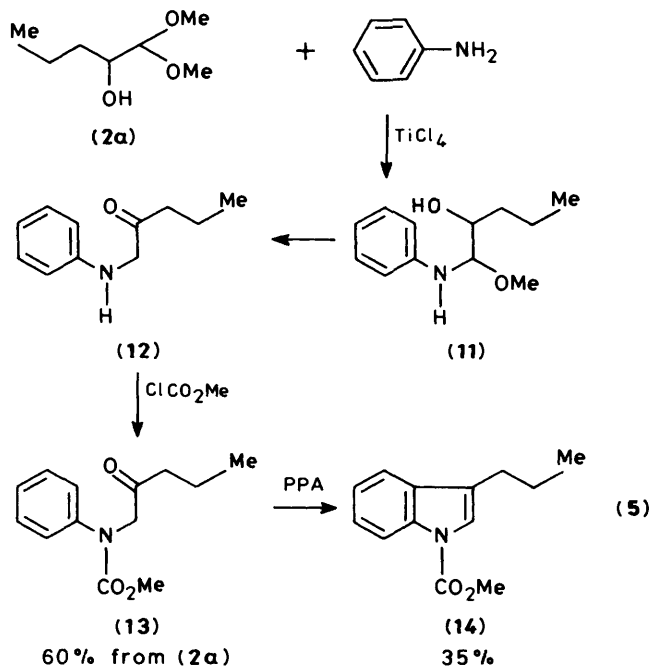
* Although electro-oxidation of carbonyl compounds under neutral conditions has been claimed in a patent, the extremely low yields reported show that this method is impractical.⁶

[†] The transformation of 2-alkoxylated oxiranes to α -hydroxy acetals has been reported.⁷



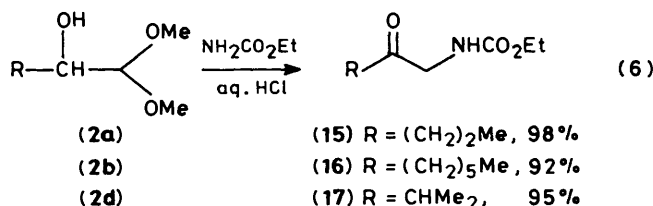
behave as the catalytic mediators in the transformation of (1) to (2). In fact, 0.5 equiv. of KI was enough to complete the oxidation of (1).

α -Hydroxy acetals (2) are versatile starting materials in organic synthesis as exemplified by the preparation of an indole derivative (14) from (2a) [Equation (5)]. Thus, the reaction of

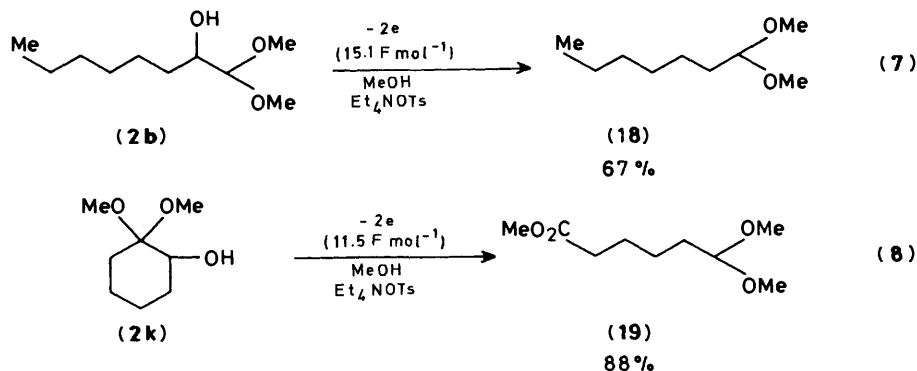


(2a) with aniline in the presence of $TiCl_4$ gave (12), presumably passing through the intermediary formation of (11). After the unstable intermediate (12) had been converted into (13), the acid catalysed intramolecular condensation of (13) yielded indole (14) as was expected.

Similarly, the β -ketoamine carbamates (15)–(17) could easily be prepared from the corresponding compound (2) [Equation (6)].



Furthermore, since carbon-carbon bond cleavage of α -hydroxylated acetals can be achieved by direct electro-oxidation in methanol,⁸ the transformation of (1) to (2) and subsequent direct electro-oxidation of (2) provide a convenient route for one-carbon shortening of aldehydes and ring-opening of cyclic ketones as exemplified in Equations (7) and (8).



Experimental

I.r. spectra were taken with a Hitachi 215 spectrometer. ^1H N.m.r. spectra were recorded on a Varian Associates EM-360 or EM-390 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University. Boiling points were uncorrected. Electro-oxidation was carried out using DC Power Supply (GP050-2) of Takasaga Seisakusho, Ltd.

Preparation of α -Hydroxylated Acetals.—General procedure for the preparation of α -hydroxy acetals (2a)—(2n) and (2n') is exemplified by the preparation of (2b) (Table, run 2). In a cell equipped with a platinum plate anode (2 cm \times 2 cm) and a carbon rod cathode (8 mm diam.) was put a solution of (1b) (4 mmol) in methanol (30 ml) containing KI (2 mmol) and KOH (4 mmol). A constant current of 0.3 A (terminal voltage *ca.* 5 V) was passed through the solution for 1.5 h (4.3 F mol $^{-1}$ of electricity) with external cooling with an ice-water bath, after which the solvent was evaporated under reduced pressure and water added to the residue. The organic portion was extracted with CH_2Cl_2 (3 \times 50 ml) and the extracts were dried (MgSO_4). Evaporation of CH_2Cl_2 afforded crude (2b) which was purified by Kugelrohr distillation (75%). A scale-up of this reaction was easily achieved by using a carbon rod anode.

Compound (2b), b.p. 88–90 $^\circ\text{C}$ (1–3 mmHg); ν_{max} (neat) 3 450, 2 925, 2 850, 1 470, 1 120, 1 070, and 970 cm^{-1} ; δ_{H} (CCl_4) 0.90 (3 H, t, *J* 6 Hz), 1.07–1.08 (10 H, m), 2.08 (1 H, br s), 3.30 (3 H, s), 3.37 (3 H, s), 3.30–3.60 (1 H, m), and 4.00 (1 H, d, *J* 6 Hz) (Found: C, 62.9; H, 11.95. $\text{C}_{10}\text{H}_{22}\text{O}_3$ requires C, 63.12; H, 11.65%).

All α -hydroxylated acetals were isolated by Kugelrohr distillation and identified by their spectroscopic data and elemental analyses.

Compound (2a), b.p. 62 $^\circ\text{C}$ (23 mmHg); ν_{max} (neat) 3 450, 2 960, 1 470, 1 120, 1 070, and 980 cm^{-1} ; δ_{H} (CCl_4) 0.93 (3 H, t, *J* 6 Hz), 1.17–1.70 (4 H, m), 2.13 (1 H, br s), 3.33 (3 H, s), 3.37 (3 H, s), 3.33–3.62 (1 H, m), and 4.00 (1 H, d, *J* 6 Hz) (Found: C, 56.7; H, 11.1. $\text{C}_7\text{H}_{16}\text{O}_3$ requires C, 56.73; H, 10.88%).

Compound (2c), b.p. 92–94 $^\circ\text{C}$ (1 mmHg); ν_{max} (neat) 3 450, 2 940, 2 860, 1 480, 1 130, 1 080, and 980 cm^{-1} ; δ_{H} (CCl_4) 0.87 (3 H, t, *J* 6 Hz), 1.05–1.70 (14 H, m), 2.00 (1 H, br s), 3.33 (3 H, s), 3.38 (3 H, s), 3.37–3.62 (1 H, m), and 4.02 (1 H, d, *J* 6 Hz) (Found: C, 65.9; H, 12.05. $\text{C}_{12}\text{H}_{26}\text{O}_3$ requires C, 66.01; H, 12.00%).

Compound (2d), b.p. 50–52 $^\circ\text{C}$ (12 mmHg); ν_{max} (neat) 3 500, 2 975, 1 480, 1 130, 1 070, and 980 cm^{-1} ; δ_{H} (CCl_4) 0.90 (3 H, t, *J* 6 Hz), 1.53–2.00 (1 H, m), 2.17 (1 H, br s), 3.33 (3 H, s), 3.37 (3 H, s), 3.18–3.55 (1 H, m), and 4.10 (1 H, d, *J* 6 Hz) (Found: C, 56.45; H, 11.15. $\text{C}_7\text{H}_{16}\text{O}_3$ requires C, 56.73; H, 10.88%).

Compound (2e), b.p. 73–75 $^\circ\text{C}$ (10 mmHg); ν_{max} (neat) 3 470, 2 970, 2 940, 1 470, 1 120, 1 080, and 960 cm^{-1} ; δ_{H} (CCl_4) 0.87 (6

H, t, *J* 7 Hz), 1.50 (4 H, q, *J* 7 Hz), 1.73 (1 H, br s), 3.48 (6 H, s), and 4.03 (1 H, s) (Found: C, 59.1; H, 11.35. $\text{C}_8\text{H}_{18}\text{O}_3$ requires C, 59.23; H, 11.18%).

Compound (2f), b.p. 90–91 $^\circ\text{C}$ (1 mmHg); ν_{max} (neat) 3 470, 2 950, 1 460, 1 110, 1 080, and 970 cm^{-1} ; δ_{H} (CCl_4) 0.80–1.03 (3 H, m), 0.83 (3 H, t, *J* 6 Hz), 1.47 (2 H, q, *J* 6 Hz), 1.10–1.45 (6 H, m), 1.82 (1 H, br s), 3.43 (6 H, s), and 4.00 (1 H, s) (Found: C, 63.2; H, 11.9. $\text{C}_{10}\text{H}_{22}\text{O}_3$ requires C, 63.12; H, 11.65%).

Compound (2g), b.p. 85–90 $^\circ\text{C}$ (3 mmHg); ν_{max} (neat) 3 470, 2 930, 2 850, 1 450, 1 080, and 970 cm^{-1} ; δ_{H} (CCl_4) 0.93–1.87 (11 H, m), 3.42 (6 H, s), and 4.80 (1 H, s) (Found: C, 62.35; H, 10.6. $\text{C}_9\text{H}_{18}\text{O}_3$ requires C, 62.04; H, 10.41%).

Compound (2h), b.p. 96–98 $^\circ\text{C}$ (1 mmHg); ν_{max} (neat), 3 460, 3 070, 3 040, 2 950, 2 845, 1 610, 1 460, 1 090, 980, and 700 cm^{-1} ; δ_{H} (CCl_4) 2.13 (1 H, br s), 2.57 (1 H, dd, *J* 7.5 and 13.5 Hz), 2.87 (1 H, dd, *J* 3 and 13.5 Hz), 3.31 (6 H, s), 3.57–3.87 (1 H, m), 4.03 (1 H, d, *J* 6 Hz), and 7.20 (5 H, br s) (Found: C, 67.1; H, 8.35. $\text{C}_{11}\text{H}_{16}\text{O}_3$ requires C, 67.32; H, 8.22%).

Compound (2i), b.p. 100–102 $^\circ\text{C}$ (1 mmHg); ν_{max} (neat) 3 530, 3 040, 2 990, 2 880, 1 480, 1 140, 1 115, 1 010, and 735 cm^{-1} ; δ_{H} (CCl_4) 1.40 (3 H, s), 2.38 (1 H, br s), 3.20 (3 H, s), 3.37 (3 H, s), 4.03 (1 H, s), and 7.00–7.53 (5 H, m) (Found: C, 67.2; H, 8.15. $\text{C}_{11}\text{H}_{16}\text{O}_3$ requires C, 67.32; H, 8.22%).

In the oxidation of (1i), 2-methoxy-3-methyl-3-phenyl-oxirane (10) was also obtained as a by-product in 26% yield.

Compound (10), ν_{max} (neat) 2 945, 1 500, 1 470, 1 450, 1 218, 1 105, 760, and 700 cm^{-1} ; δ_{H} (CCl_4) 1.67 (3 H, s), 3.55 (3 H, s), 4.20 (1 H, s), and 7.32 (5 H, s) (Found: M^+ , 164.0818. $\text{C}_{10}\text{H}_{12}\text{O}_2$ requires M , 164.0837).

Compound (2j), ν_{max} (neat) 3 500, 2 960, 1 740, 1 440, 1 200, 1 165, 1 135, 1 080, and 975 cm^{-1} ; δ_{H} (CCl_4) 1.17–1.95 (4 H, m), 2.05 (1 H, br s), 2.18–2.42 (3 H, m), 3.37 (3 H, s), 3.40 (3 H, s), 3.62 (3 H, s), and 4.03 (2 H, d, *J* 6.0 Hz) (Found: C, 52.3; H, 8.7. $\text{C}_9\text{H}_{18}\text{O}_5$ requires C, 52.41; H, 8.80%).

Compound (2k), b.p. 76–78 $^\circ\text{C}$ (5 mmHg); ν_{max} (neat) 3 480, 2 960, 1 460, 1 110, 1 060, and 890 cm^{-1} ; δ_{H} (CCl_4) 1.10–1.93 (8 H, m), 2.25 (1 H, br s), 3.22 (6 H, s), and 3.70–3.87 (1 H, m) (Found: C, 60.25; H, 10.2. $\text{C}_8\text{H}_{16}\text{O}_3$ requires C, 59.98; H, 10.07%).

Compound (2l), b.p. 80–82 $^\circ\text{C}$ (5 mmHg); ν_{max} (neat) 3 475, 2 955, 1 470, 1 130, 1 090, 955, 840, and 695 cm^{-1} ; δ_{H} (CCl_4) 1.48–2.07 (2 H, m), 2.30–3.77 (1 H, m), 3.22 (3 H, s), 3.23 (3 H, s), and 3.32–3.85 (5 H, m) (Found: C, 51.55; H, 9.0. $\text{C}_7\text{H}_{14}\text{O}_4$ requires C, 51.83; H 8.70%).

Compound (2m), b.p. 88–90 $^\circ\text{C}$ (1 mmHg); ν_{max} (neat) 3 495, 2 970, 1 470, 1 390, 1 055, and 880 cm^{-1} ; δ_{H} (CCl_4) 1.13 (3 H, s), 1.28 (3 H, t, *J* 7 Hz), 1.03–1.77 (8 H, m), 1.90 (1 H, br s), 3.20 (3 H, s), 3.23 (3 H, s), and 3.42–3.83 (1 H, m) (Found: C, 62.95; H, 11.75. $\text{C}_{10}\text{H}_{22}\text{O}_3$ requires C, 63.12; H, 11.65%).

Anodic oxidation of 2-methylcyclohexanone (1n) gave a mixture of 2-hydroxy-2-methylcyclohexanone (2n) and 2-

methyl-6-hydroxycyclohexanone (**2n'**). The ratio (82:18) of (**2n**) and (**2n'**) was determined by g.l.c., and their isolation was achieved by p.l.c. (77% yield).

Compound (2n), ν_{\max} (neat) 3 500, 2 950, 1 463, 1 100, 1 060, 1 020, and 960 cm^{-1} ; δ_{H} (CCl_4) 1.17 (3 H, s), 1.07—2.05 (8 H, m), 2.27 (1 H, br s), 3.25 (3 H, s), and 3.32 (3 H, s) (Found: C, 62.0; H, 10.2. $\text{C}_9\text{H}_{18}\text{O}_3$ requires C, 62.04; H, 10.41%).

Compound (2n'), ν_{\max} (neat) 3 480, 2 950, 1 463, 1 120, 1 060, and 950 cm^{-1} ; δ_{H} (CCl_4) 1.10 (3 H, d, J 8 Hz), 1.07—2.18 (7 H, m), 2.27 (1 H, br s), 3.17 (3 H, s), 3.25 (3 H, s), and 3.70—4.00 (1 H, m) (Found: C, 62.0; H, 10.25. $\text{C}_9\text{H}_{18}\text{O}_3$ requires C, 62.04; H, 10.41%).

Synthesis of the Indole (14).—To a stirred solution of (**2a**) (5 mmol) in CH_2Cl_2 (10 ml) was added dropwise TiCl_4 (7.5 mmol) under an atmosphere of nitrogen at -50°C . After the solution had been stirred for 5 min with external cooling, aniline (10 mmol) was added dropwise, and the resulting solution was stirred for 2 h at room temperature. An aqueous solution of KOH was added to the reaction mixture until the solution became basic, and it was then extracted with CH_2Cl_2 (3×50 ml). The extracts were dried (MgSO_4), and the solvent (*ca.* 100 ml) removed under reduced pressure. K_2CO_3 (20 mmol) was added to the residue and subsequently methyl chloroformate (15 mmol) dropwise at 0°C . The resulting solution was stirred for 1 h at room temperature, after which the white precipitate was filtered off and the solvent evaporated under reduced pressure to give a residue. This was subjected to silica gel column chromatography (AcOEt—hexane, 1:10) to afford (**13**) (60% yield), ν_{\max} (neat) 2 950, 1 710, 1 600, 1 500, 1 445, 1 380, 1 210, 1 160, 770, and 700 cm^{-1} ; δ_{H} (CCl_4) 0.93 (3 H, t, J 7 Hz), 1.20—2.07 (2 H, m), 2.37 (2 H, t, J 7 Hz), 3.67 (3 H, s), 4.30 (2 H, s), and 7.33 (5 H, br s) (Found: C, 66.3; H, 7.35; N, 5.85. $\text{C}_{13}\text{H}_{17}\text{NO}_3$ requires C, 66.36; H, 7.28; N, 5.95%).

A mixture of (**13**) (1.6 mmol) and PPA (3 ml) was heated at 140°C for 20 min under an atmosphere of nitrogen. After cooling to 0°C , the solution was made basic (pH 8—10) with aqueous KOH with external cooling in ice-water, and the organic portion was extracted with CH_2Cl_2 (3×50 ml). The combined extracts were dried (MgSO_4), and evaporated under reduced pressure to give a residue, which was subjected to silica gel column chromatography (AcOEt—hexane, 1:10) to afford (**14**) (35%), ν_{\max} (neat) 2 975, 1 740, 1 390, 1 260, 1 110, 770, and 750 cm^{-1} ; δ_{H} (CCl_4) 1.00 (3 H, t, J 7 Hz), 1.37—2.15 (2 H, m), 2.70 (3 H, t, J 7 Hz), 4.02 (3 H, s), 7.11—7.80 (4 H, m), and 7.98—8.53 (1 H, m) (Found: C, 71.8; H, 7.0; N, 6.3. $\text{C}_{13}\text{H}_{15}\text{NO}_2$ requires C, 71.86; H, 6.96; N, 6.45%).

Preparation of N-Methoxycarbonyl- β -ketoamines (15)—(17).—The general procedure for the preparation of *N*-methoxycarbonyl- β -ketoamines is exemplified by the preparation of (**16**).

To a stirred solution of (**2b**) (14.5 mmol) and ethyl carbamate (29 mmol) in benzene (100 ml) was added concentrated HCl (2 ml), and the resulting solution was refluxed for 1 h. After treatment with saturated NaHCO_3 (50 ml), the reaction mixture was extracted with CH_2Cl_2 (3×100 ml), and the combined extracts were dried (MgSO_4) and evaporated under reduced pressure. The residue was distilled under reduced pressure to afford (**16**) (92%).

Compound (15), b.p. $135\text{--}138^\circ\text{C}$ (1 mmHg); ν_{\max} (neat) 3 370, 2 970, 1 710, 1 530, 1 380, 1 255, 1 180, 1 030, and 780 cm^{-1} ; δ_{H} (CCl_4) 0.95 (3 H, t, J 7 Hz), 1.23 (3 H, t, J 7 Hz), 1.47—1.93 (2 H, m), 2.42 (2 H, t, J 7 Hz), 3.93 (2 H, d, J 4 Hz), 4.03 (2 H, q, J 7 Hz), and 5.25—5.70 (1 H, m) (Found: C, 55.2; H, 8.5; N, 8.1. $\text{C}_8\text{H}_{15}\text{NO}_3$ requires C, 55.47; H, 8.73; N, 8.09%).

Compound (16), b.p. $155\text{--}158^\circ\text{C}$ (1 mmHg, m.p. $34.0\text{--}35.0^\circ\text{C}$ (from hexane); ν_{\max} (KBr) 3 325, 2 930, 1 720, 1 695, 1 555, 1 285, 1 180, 1 050, and 780 cm^{-1} ; δ_{H} (CCl_4) 0.90 (3 H, t, J

7 Hz), 1.13—1.88 (8 H, m), 1.23 (3 H, t, J 8 Hz), 2.42 (3 H, t, J 7 Hz), 3.95 (2 H, d, J 4 Hz), 4.05 (2 H, q, J 8 Hz), and 5.20—5.63 (1 H, m) (Found: C, 61.5; H, 10.15; N, 6.6. $\text{C}_{11}\text{H}_{21}\text{NO}_3$ requires C, 61.37; H, 9.83; N, 6.51%).

Compound (17), b.p. $130\text{--}133^\circ\text{C}$ (1 mmHg); m.p. $39.5\text{--}40.0^\circ\text{C}$ (from hexane); ν_{\max} (neat) 3 370, 2 980, 1 740, 1 720, 1 695, 1 540, 1 280, and 1 035 cm^{-1} ; δ_{H} (CCl_4) 1.17 (6 H, d, J 7 Hz), 1.22 (3 H, t, J 7 Hz), 2.40—2.88 (1 H, m), 4.05 (2 H, d, J 3 Hz), 4.07 (2 H, q, J 7 Hz), and 5.27—5.73 (1 H, m) (Found: C, 55.45; H, 8.8; N, 8.05. $\text{C}_8\text{H}_{15}\text{NO}_3$ requires C, 55.47; H, 8.73; N, 8.09%).

Anodic Oxidation of (2b) and (2k).—The general procedure for the anodic oxidation of (**2b**) and (**2k**) is exemplified by the oxidation of (**2b**). In an undivided cell equipped with carbon rod electrodes was placed a solution of (**2b**) (4 mmol) in methanol (30 ml) containing TsONeEt_4 (100 mg) as a supporting electrolyte. A constant current of 0.3 A was passed through the solution for 5.4 h (15.1 F mol^{-1} of electricity) with external cooling with ice-water, after which the solvent was evaporated under reduced pressure. Aqueous K_2CO_3 was added to the residue which was then extracted with CH_2Cl_2 (3×50 ml). The combined extracts were dried (MgSO_4) and evaporated under reduced pressure to give a residue, which was purified by Kugelrohr distillation to afford heptaldehyde dimethyl acetal (**18**) (67%); the yield of (**19**) was 88%. Identification of (**18**) and (**19**) was achieved by comparison of their spectroscopic data with those of authentic samples.⁹ **Compound (18)**, ν_{\max} (neat) 2 945, 2 860, 1 470, 1 125, and 1 070 cm^{-1} ; δ_{H} (CCl_4) 0.88 (3 H, t, J 7 Hz), 1.10—1.75 (10 H, m), 3.77 (6 H, s), and 4.25 (1 H, t, J 5 Hz). **Compound (19)**, ν_{\max} (neat) 2 950, 1 742, 1 440, 1 130, 1 080, and 960 cm^{-1} ; δ_{H} (CCl_4) 1.10—1.87 (6 H, m), 2.28 (2 H, t, J 7 Hz), 3.23 (6 H, s), 3.64 (3 H, s), and 4.26 (1 H, s, J 6 Hz).

Acknowledgements

We thank the Ministry of Education, Science, and Culture, Japan for a Grant-in-Aid for Special Project Research (1) (No. 57118003, 58110003, and 59104003) (to T.S.) and for a Grant-in-Aid for Developmental Scientific Research (2) (No. 58850178) (to Y.M.).

References

- 1 Electro-organic Chemistry. Part 93. A part of this study has been presented at the 1984 International Chemical Congress Pacific Basin Societies, Honolulu, December 17, 1984.
- 2 (a) G. M. Rubottom, M. A. Vazquez, and D. R. Pelegrina, *Tetrahedron Lett.* 1974, **15**, 4319; (b) T. Shono, M. Okawa, and I. Nishiguchi, *J. Am. Chem. Soc.*, 1975, **97**, 6144; (c) T. Shono, I. Nishiguchi, and M. Nitta, *Chem. Lett.*, 1976, 1319; (d) F. Huet, A. Lechevallier, and J. M. Conia, *Synth. Commun.*, 1980, **10**, 83; (e) M.-P. Strobel, L. Morin, and D. Paquer, *Tetrahedron Lett.*, 1980, **21**, 523; (f) E. Friedrich and W. Lutz, *Chem. Ber.*, 1980, **113**, 1245; (g) C. H. Cummins and R. M. Coates, *J. Org. Chem.*, 1983, **48**, 2070, and references cited therein.
- 3 (a) R. M. Moriarty, S. C. Gupta, H. Hu, D. R. Berenschot, and K. B. White, *J. Am. Chem. Soc.*, 1981, **103**, 686; (b) R. M. Moriarty, L. S. John, and P. C. Du, *J. Chem. Soc., Chem. Commun.*, 1981, 641; (c) R. M. Moriarty and K.-C. Hou, *Tetrahedron Lett.*, 1984, **25**, 691.
- 4 (a) T. Shono, Y. Matsumura, J. Hayashi, M. Mizoguchi, *Tetrahedron Lett.*, 1979, **20**, 165; (b) *ibid.*, 1979, **20**, 3861; (c) *ibid.*, 1980, **21**, 1867; (d) T. Shono, Y. Matsumura, S. Yamane, and S. Kashimura, *Chem. Lett.*, 1982, 565; (e) T. Shono, Y. Matsumura, and K. Inoue, *J. Org. Chem.*, 1983, **48**, 1388; (f) T. Shono, Y. Matsumura, J. Hayashi, M. Usui, S. Yamane, and K. Inoue, *Acta Chem. Scand., Ser. B*, 1983, **37**, 491; (g) T. Shono, Y. Matsumura, and K. Inoue, *J. Chem. Soc., Chem. Commun.*, 1983, 1169; (h) T. Shono, *Tetrahedron*, 1984, **40**, 811.
- 5 T. Shono, Y. Matsumura, J. Hayashi, K. Inoue, F. Iwasaki, and T. Itoh, *J. Org. Chem.*, in the press.
- 6 H. Watanabe, Japan Kokai, 72892 (1981).

- 7 (a) A. Hassner, R. H. Reuss, and H. W. Pinnick, *J. Org. Chem.*, 1975, **40**, 3427; (b) A. A. Friemer, *Synthesis*, 1977, 578.
- 8 (a) T. Shono, Y. Matsumura, K. Hibino, H. Hamaguchi, and T. Aoki, *J. Am. Chem. Soc.*, 1975, **97**, 2546; (b) T. Shono, Y. Matsumura, H. Hamaguchi, T. Imanishi, and K. Yoshida, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2179.
- 9 R. C. Cookson, N. W. Hughes, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2738.

Received 15th April, 1985; Paper 5/627