mg, 12%), dimethyl phthalate (3.1 mg, 16%), and **6** (13 mg, 41%). Recrystallization of **7** gave pale yellow prisms: mp 216 °C dec; IR ($CDCl_3$) ν_{max} 1672 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.10 (1 H, d, J = 6.0 Hz), 2.00 (1 H, d, J = 6.0 Hz), 5.17 (2 H, s), 6.32 (2 H, s), 6.95–7.50 (8 H, m); MS (7.5 eV), m/z (relative intensity) 298 (M^+, 86), 216 (86), 215 (100), 178 (28). Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.22; H, 4.86.

Electrochemical Transformations of Aldehydes into Methyl Carboxylates and Nitriles

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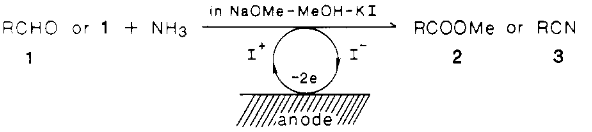
The one-step transformation of aldehydes (**1**) into the corresponding methyl carboxylates (**2**) or nitriles (**3**) appears to be an attractive synthetic process. Although several methods have been reported for the direct preparation of **2** from **1**,[1] or **3** from **1** with ammonia,[2] they usually require large amounts of reagents, elevated temperature, and/or a lengthy reaction period. We describe in this paper an efficient procedure for obtaining **2** or **3** from **1** by means of indirect electrooxidation using a redox system of iodide ions as a mediator.[3]

Results and Discussion

The electrooxidative preparation of **2** from **1** was conducted in MeOH containing NaOMe and a catalytic amount of KI, whereas for the preparation of **3** excess ammonia was further added to the electrolyte system. All of the electrolyses were carried out in a divided cell with a platinum anode under a constant current until a yield of desired product reached its maximum value. The results of electrolyses are summarized in Table I.



Preparation of 2. As shown in the table, this method gave good results with aromatic aldehydes. In each case, almost all of the quantity of **1** was converted into **2** at the stage where the theoratical amount of electricity (2 F/mol of **1**) has passed through. The yield of the substituted methyl benzoates was hardly affected by the steric and electronic effects of the substituents. Aliphatic aldehydes having an α-hydrogen atom were not applicable, because of aldol condensation.

An exellent catalytic behavior was also observed with NaI, $(Et)_4NI$, and I_2, but other alkali halide such as KBr or KCl did not show their effects for converting **1** into **2**. The presence of NaOMe as a strong base and the separation of the anolyte from catholyte were essential in order to obtain satisfactory yields of **2**. For example, the electrolysis with benzaldehyde in an undivided cell gave only about a 48% yield of methyl benzoate even when 0.5 equiv of KI for **1** was used, and no **2** was formed when the electrolysis was carried out without NaOMe in a divided cell by using a neutral salt such as $NaClO_4$ or $(Et)_4OTs$ as the supporting electrolyte together with KI. In these cases, the dimethyl acetal of **1** was formed. Probably, the corresponding acid generated at the anode and catalyzed the acetal formation.

Table I. Electrochemical Transformation of Aldehydes into Methyl Carboxylates[a] or Nitriles[b]

RCHO, R	electricity passed, F/mol	yield of ester,[c] %	electricity passed, F/mol	yield of nitrile,[c] %
C_6H_5	2.0	80	2.5	73
2-$CH_3C_6H_4$	2.2	84	2.6	86
4-$CH_3C_6H_4$	2.1	82	2.6	90
2-$CH_3OC_6H_4$	2.6	78	2.8	70
4-$CH_3OC_6H_4$	2.1	86	2.8	90
2-ClC_6H_4	2.2	83	2.6	88
4-ClC_6H_4	2.0	87	2.2	85
2-$NO_2C_6H_4$	2.1	70	2.0	0[f]
4-$NO_2C_6H_4$	2.0	91	2.0	0[f]
2-furyl	2.0	70	2.2	trace[d]
1-naphthyl	2.1	84	2.4	54
$(CH_3)_2(HOCH_2)C$	2.0	68	2.2	55
n-C_3H_7			3.3	59[e]
n-C_5H_{11}			3.0	50
n-C_7H_{15}	2.0	0[f]	2.2	66
$CH_3(CH_2)_3(C_2H_5)CH$	2.0	0[f]	3.0	70
cyclo-C_6H_{11}			2.1	48

[a] Anolyte: aldehyde (50 mmol) and KI (5 mmol) in MeOH (80 mL) containing NaOMe (10 mmol). Constant current: 0.5 A. Temperature: ca. 17 °C. [b] Anolyte: aldehyde (50 mmol), KI (10 mmol), and NH_3 (380 mmol) in MeOH (80 mL) containing NaOMe (10 mmol). Constant current: 0.5 A. Temperature: ca. 5 °C. [c] Isolated yield based on **1**. [d] Methyl furimidate was obtained in a yield of 60%: bp 67–69 °C (19 mm); IR (neat) 3320 (NH), 1655 cm^{-1} (C=NH); ^1H NMR ($CDCl_3$) δ 3.91 (s, 3, OCH_3), 6.47 (dd, 1, J = 3 Hz, furan ring), 6.78 (dd, 1, J = 3 Hz, furan ring), 7.50 (dd?, 1, furan ring), 7.71 (s, 1, NH); MW 125 (mass). [e] Determined by GLC. [f] Unidentified products were formed.

In material yield, current efficiency, and ease of experimental manipulation, the present method was superior to our previous one using a NaCN–MeOH electrolyte system.[1]

Preparation of 3. Analogously, the electrochemical preparation of **3** was successfully performed with aromatic aldehydes in the presence of excess ammonia. To suppress the formation of undesirable **2**, a large excess of ammonia and a small amount of NaOMe were used. Under the present condition, no or little **2** was formed in most cases.

From furfural, methyl furimidate was obtained as the main product along with a small amount of furonitrile. It is highly probable that the produced furonitrile was solvolyzed with MeOH in the presence of NaOMe. In fact, furonitrile was readily converted into methyl furimidate by treatment with NaOMe–MeOH at room temperature.[4] Nitrobenzaldehydes afforded intractible mixtures, which did not contain the expected **3**.

With similar ease, aliphatic aldehydes could also be transformed into **3**, although in somewhat lower yields. The decrease in the yield may be partly ascribed to an aldol condensation. In these cases, highly viscous liquids remained after distillation of the products.

Thus, it can be said that a catalytic amount of KI promoted both transformation reactions. In these electrolyte systems, the iodide anion is most readily electrooxidized,[5]

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(1) For our previous report on the electrooxidative conversion of **1** into **2**, see: Chiba, T.; Okimoto, M.; Nagai, H.; Takata, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 335 and references cited therein.

(2) (a) Parameswaren, K. N.; Friedman, O. M. *Chem. Ind.* (*London*) **1965**, 988. (b) Brackman, W.; Smit, P. J. *Recl. Trav. Chim. Pay-Bas* **1963**, *82*, 757. (c) Misono, A.; Osa, T.; Koda, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 854. (d) Nakagawa, K.; Onoue, H.; Minami, K. *J. Chem. Soc., Chem. Commun.* **1966**, 17. See also: Ganboa, I.; Palomo, C. *Synth. Commun.* **1983**, *13*, 219.

(3) For a review of oxidation using halide ion as the mediator, see: Shono, T. *Tetrahedron* **1984**, *40*, 811.

(4) For example, see: Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*; Academic: New York, 1972; Vol. 3, Chapter 8.

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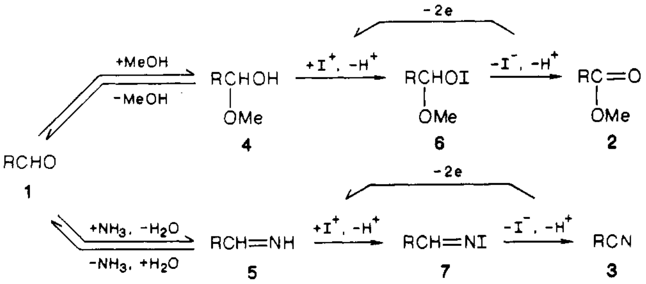
and therefore it is reasonable to assume that the actual oxidizing agent was a positive iodine species generated electrochemically, which formed a redox system with iodide anions.[6]

The analogous chemical reaction of **1** with I_2 in ammoniacal methanol has been reported to give **2** and **3**.[7] We also observed that the reaction of **1** with I_2 in NaOMe–MeOH gave **2** in contrast to a mixture of **3** and **2** in NaOMe–MeOH–NH_3,[8] in which the relative yield of **3** to **2** decreased with increasing the amount of NaOMe.[9] Moreover, at least an equimolecular amount of I_2 and sufficient base to neutralize the HI formed were required to complete these reactions.

From the above observations, the course of the present electrochemical reaction seems to resemble that of the chemical reaction with I_2. Generally, **1** and alcohols are known to form equilibrium mixtures with the hemiacetals (**4**), and the formation of **4** is catalyzed by both acid and base.[10] Also, **1** readily reacts with ammonia to give aldimines (**5**).[2b] Consequently, the reaction path may be represented as follows:



The positive iodine species generated by electrochemical oxidation of I^- attacks **4** or **5** to give an intermediate such as **6** or **7**, which then undergoes an elimination of HI by base to afford the corresponding product **2** or **3**, and the resulting I^- is reoxidized at the anode. In the electrolyte system employed for the preparation of **3**, the equilibrium must lie far to the aldimine side, since **1** were predominantly converted into **3**. In addition, **5** is presumed to be more oxidizable than **6**.

It may be concluded that the overall electrochemical reaction involves the in situ generation of positive iodine species which then gets involved in the production of **2** and **3**. By the electrochemical method, **1** could effectively be converted into **2** or **3** by using small amounts of reagents which are readily available and inexpensive, particularly aromatic aldehydes.

Experimental Section

Preparative electrolyses were carried out in a 100-mL separable flask equipped with a fine frits cup as the cathode compartment, a cylindrical platinum net anode, and a nickel coil cathode.

General Procedure for the Preparation of 2. A solution of aldehyde (50 mmol) and KI (5 mmol) in MeOH (80 mL) containing NaOMe (10 mmol) was electrooxidized under a constant current of 0.5 A (the terminal voltage was ca. 10 V). As the catholyte, the same concentration of NaOMe–MeOH was used. During the electrolysis, the anolyte was stirred with a magnetic stirring bar, and the cell was cooled with running water. The progress of the reaction was followed by GLC analyses of the anolyte.

After completion of the reaction, the solution in the anode compartment was concentrated under reduced pressure without heating. The residue was vigorously shaken with a saturated sodium hydrogen sulfite solution (10 mL), treated with water, and extracted with ether (3 × 25 mL). The combined ether extracts were washed with water (30 mL), dried over anhydrous sodium sulfate, and distilled under reduced pressure or recrystalized after removal of the solvent.

Preparation of 3. In a similar manner, the aldehyde (50 mmol) was dissolved in MeOH (80 mL) containing NaOMe (10 mmol), KI (10 mmol), and ammonia (380 mmol), and the resulting solution was subjected to electrooxidation at ice-bath temperature. After the electrolysis, the anolyte was worked up as above.

Products obtained were identified by comparison of their physical and spectral data with those of authentic samples or with the literature data.[11]

Registry No. Fe, 7439-89-6; H_2SO_4, 7664-93-9; 4-$CH_3C_6H_4CHO$, 104-87-0; 2-$CH_3OC_6H_4CHO$, 135-02-4; 4-$CH_3OC_6H_4CHO$, 123-11-5; 2-ClC_6H_4CHO, 89-98-5; 4-ClC_6H_4CHO, 104-88-1; 2-$NO_2C_6H_4CHO$, 552-89-6; 4-$NO_2C_6H_4CHO$, 555-16-8; $(CH_3)_2(HOCH_2)CCHO$, 597-31-9; *n*-C_6H_7CHO, 123-72-8; *n*-$C_5H_{11}CHO$, 66-25-1; *n*-C_7H_{15}, 124-13-0; $CH_3(CH_2)_3CH(C_2H_5)CHO$, 123-05-7; cyclo-$C_6H_{11}$, 2043-61-0; $C_6H_5CO_2Me$, 93-58-3; 2-$CH_3C_6H_4CO_2Me$, 89-71-4; 4-$CH_3C_6H_4CO_2Me$, 99-75-2; 2-$CH_3OC_6H_4CO_2Me$, 606-45-1; 4-$CH_3OC_6H_4CO_2Me$, 23676-09-7; 2-$ClC_6H_4CO_2Me$, 610-96-8; 4-$ClC_6H_4CO_2Me$, 1126-46-1; 2-$NO_2C_6H_4CO_2Me$, 606-27-9; 4-$NO_2C_6H_4CO_2Me$, 619-50-1; $(CH_3)_2(HOCH_2)CCO_2Me$, 14002-80-3; C_6H_5CN, 100-47-0; 2-$CH_3C_6H_4CN$, 529-19-1; 4-$CH_3C_6H_4CN$, 104-85-8; 2-$CH_3OC_6H_4CN$, 6609-56-9; 4-$CH_3OC_6H_4CN$, 874-90-8; 2-ClC_6H_4CN, 873-32-5; 4-ClC_6H_4CN, 623-03-0; $(CH_3)_2(HOCH_2)CCN$, 19295-57-9; *n*-C_3H_7CN, 109-74-0; *n*-$C_5H_{11}CN$, 628-73-9; *n*-$C_7H_{15}CN$, 124-12-9; $CH_3(CH_2)_3CH(C_2H_5)CN$, 4528-39-6; cyclo-$C_6H_{11}CN$, 766-05-2; KI, 7681-11-0; NaI, 7681-82-5; $(Et)_4NI$, 68-05-3; I_2, 7553-56-2; MeOH, 67-56-1; NaOMe, 124-41-4; NH_3, 7664-41-7; 2-furancarboxaldehyde, 98-01-1; 1-naphthylenecarboxaldehyde, 66-77-3; methyl 2-furancarboxylate, 611-13-2; methyl 1-naphthylenecarboxylate, 2459-24-7; methyl furimidate, 51282-48-5; 1-naphthylenenitrile, 86-53-3.

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(6) (a) Miller, L. L.; Watkins, B. F. *Tetrahedron Lett.* **1974**, 4495. (b) Shono, T.; Matsumura, Y.; Inoue, K.; Iwasaki, F. *J. Chem. Soc., Perkin Trans. 1* **1986**, 73.

(7) Misono, A.; Osa, T.; Koda, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2875.

(8) If no NaOMe is used, the former reaction does not occur, and the latter is extreamly slow and gives very poor yields of **2** and **3**.

(9) An addition of I_2 to ammoniacal methanol sometimes resulted in a sudden explosion. Therefore, the treatment of I_2 with ammonia was deemed to highly dangerous, especially on a large scale, because of the formation of the explosive nitrogen triiodide. See: Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic: New York, 1963; P 480.

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(11) Pollack, J. R. A.; Stevens, R. *Dictionary of Organic Compounds*; Eyre and Spottiswoode Ltd: Great Britain, 1965.

Concerning the Reported Photosolvolysis of 4-Chloro-2-butanone in Alcoholic Media[1]

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In 1970, Kossanyi and Mogto[2] reported the photoreaction of 4-chloro-2-butanone (**4-CB**) in several alcoholic solvents. Two products were obtained, the anticipated alcohol resulting from carbonyl photoreduction plus the

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