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Author(s)	Satoh, Shohei; Itoh, Mitsuomi; Suginome, Hiroshi et al.
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Electrochemical Reduction of Dimethyl 2, (ω−1) -Dibromoalkanedioates : A Convenient Synthesis of Cycloalkane-1, 2-dicarboxylic Acid Esters

Shohei SATOH,* *the late* Mitsuomi ITOH,* Hiroshi SUGINOME* and Masao TOKUDA*

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Abstract

Constant current electrolyses of dimethyl 2, (ω-1) -dibromoalkanedioates **(1)** in tetrahydrofuran containing tetrabutylammonium perchlorate as a supporting electrolyte using a platinum cathode afforded the corresponding *trans* and *cis* dimethyl cycloalkane-1, 2-dicarboxylates **(2)** in moderate to good yields. Three to seven-membered ring cycloalkanes **(2)** can be prepared by this electrolysis. The solvent, cathode material and electrolysis potential were found to affect appreciably the ratios of the *trans* and *cis* isomers. The electrolysis of dimethyl 2, 4-dibromopentanedioate **(1a)** using a mercury pool as a cathode gave the corresponding cycloalkane **2a** in a lower yield and the product was accompanied by a large amount of open-chain esters. The present electrolysis probably proceeds *via* a two electron reduction of one of the carbon-bromine bonds of dibromoalkanedioates **(1)** to generate a carbanion which then undergoes an intramolecular nucleophilic attack on a carbon bearing bromine atom.

1. Introduction

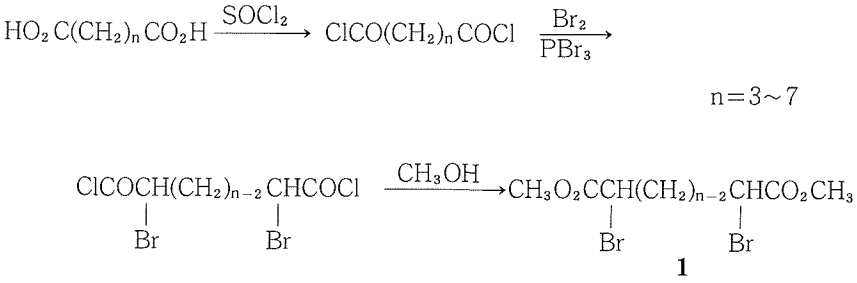
The electrochemical reduction of carbon-halogen bonds has been extensively studied although the application for organic synthesis has only recently begun.[1] The cleavage of a carbon-halogen bond of monohalo compounds by cathodic reduction generally gives radical or carbanion, which can lead to the formation of the corresponding coupling products or hydrocarbons. Reduction of α, ω−dihalides in general proceeds in a stepwise manner through anionic intermediates to yield the cyclic products. Thus, electrochemical reduction of 1, 3-dibromopropane in dimethylformamide (DMF) containing tetraethylammonium bromide gives cyclopropane in over 80% yield[2-4] : 1, 2-Dimethylcyclopropane,[5] phenylcyclopropane,[6] and cyclopropanol[6] are formed from the corresponding dihalides ; bicyclobutane and dimethylbicyclobutane are produced in 60-90% yields by electrochemical reductions of 1-bromo-3-chlorocyclobutane and 1, 3-dibromo-1, 3-dimethylcyclobutane[2,3] ; spiropentane and other strained cyclopropanes are also obtained[2,3,7]. Electrochemical reduction of 1, 4-dibromobutane gives cyclobutane and n-butane in a 1 : 3 ratio[2,3] but electrolysis at more negative potential gives only cyclodutane in a 70% yield.[4] However, preparations of higher cycloalkanes have not been possible by electrochemical reduction of simple α, ω−dihalides. In this paper we report an electrochemical reduction of 1, ω−dibromides bearing alkoxycarbonyl groups at both termini

* Division of Organic Synthesis, Department of Chemical Process Engineering

which produces three to seven-membered ring cycloalkanes in moderate yields.[8] This electrochemical cyclization provides a convenient means of synthesis of cycloalkane-1, 2-dicarboxylic acid esters which are not readily accessible by other methods.

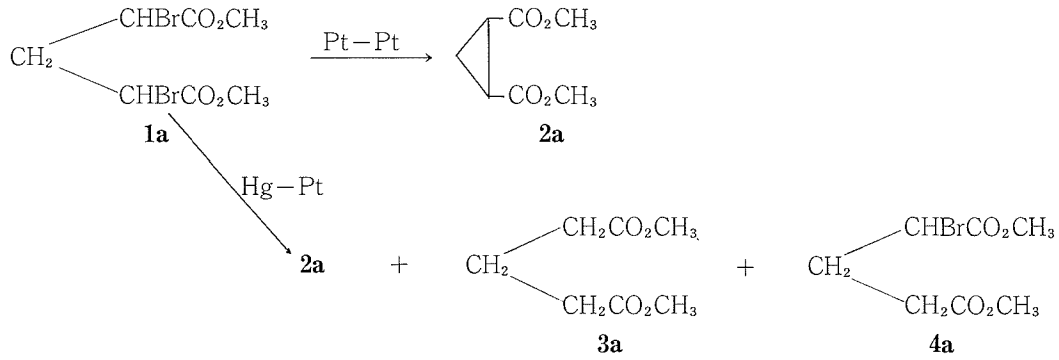
2. Results and Discussion

Starting α, α'-dibromo esters **(1)** were readily prepared by a three step procedure from the corresponding alkanedioic acid in about an 80% yield (Scheme 1).

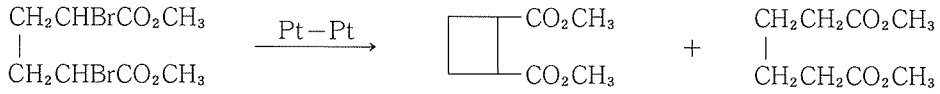


Scheme 1

Electrolysis of dimethyl 2, 4-dibromopentanedioate **(1a)** in tetrahydrofuran(THF) containing tetraalkylammonium salt as a supporting electrolyte yielded dimethyl cyclopropane-1, 2-dicarboxylate **(2a)** in a good yield (Scheme 2). Reactions were carried out in a normal undivided cell with two platinum plate electrodes. Electrolysis of dimethyl 2, 5-dibromohexanedioate **(1b)** under the same conditions as in **1a** similarly gave dimethyl cyclobutane-1, 2-dicarboxylate **(2b)** accompanied by a small amount of dimethyl hexanedioate **(3b)** (Scheme 3).



Scheme 2

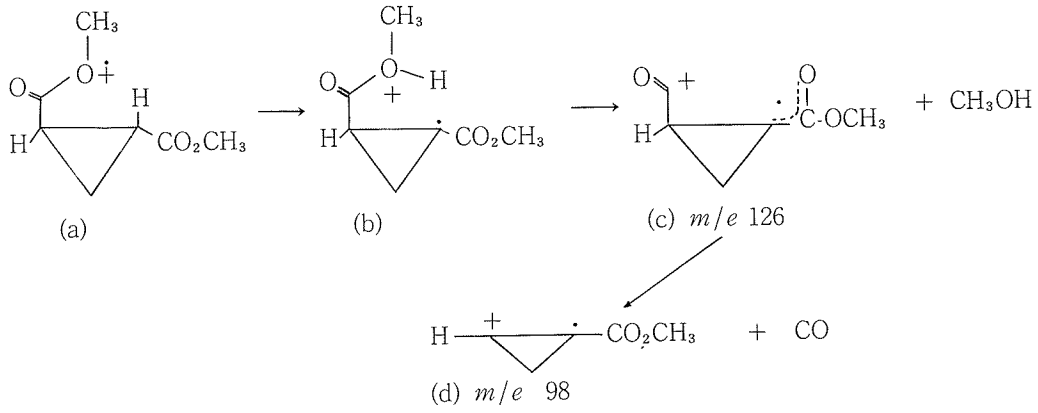


1b **2b** **3b**

Scheme 3

A change of electrolytic conditions was found to result in different yields of cyclized products **2a** and **2b** The yields of cycloalkanes **2** under various conditions of electrolysis are summarized in Table 1.

The cycloalkane **2** obtained by the electrochemical reduction is a mixture of *trans*- and *cis*-isomers as can be shown by the presence of two peaks in g. l. p. c. analysis (carbowax 20 M, 15%). The two isomers of **2a** were separated by preparative g. l. p. c. The NMR spectrum of an isomer having a shorter retention time showed a 6H singlet at δ 3.60 due to two methoxycarbonyl groups, a 2H multiplet at δ 1.27 assignable to a methylene protons of cyclopropane ring and a 2H multiplet at δ 2.00 assignable to two methine protons. The signal positions and their couplings were identical with those reported for *trans*-dimethylcyclopropane-1, 2-dicarboxylate.[9] Another isomer having a longer retention time should then be a *cis*-isomer and the NMR spectrum which showed a 6H singlet at δ 3.57 (two methoxycarbonyl groups), two 1H multiplets at δ 1,09 and 1.53 (a cyclopropyl methylene protons), and a 2H multiplet at δ 1.87 (a superimposed signal due to cyclopropyl methine protons), was in accord with this assignment. The fragmentations in mass spectra of *trans*- and *cis*-isomer of **2a** also supported these assignments. Thus, the mass spectra of both *trans* and *cis* isomers of **2a** showed their base peak at *m/e* 127 (M^+-OCH_3) and fragment ions at *m/e* 126 and *m/e* 98. The latter two fragments are assignable to species (M^+-CH_3OH) and (M^+-CH_3OH-CO) and their genesis is shown in Scheme 4. It was found that the ratio of intensity of (M^+-CH_3OH) ion to (M^+-OCH_3) ion in the *trans* isomer was significantly greater than that in the *cis* isomer. Likewise, the ratio of



Scheme 4

intensity of ($M^+-HCO_2CH_3$) ion at *m/e* 98 to ($M^+-CO_2CH_3$) ion at *m/e* 99 was greater in the *trans* isomer than in the *cis* isomer. These differences of the relative intensities can only be explained if an isomer which shows the greater ratio of intensities is assigned as *trans* isomer. Namely, an intramolecular transfer of a more mobile hydrogen attached to a carbon from the molecular ion (a) to give species (b) is apparently facilitated in the *trans* isomer in which the methoxycarbonyl group and a hydrogen to be transfered are in a *cis* relationship.[10]

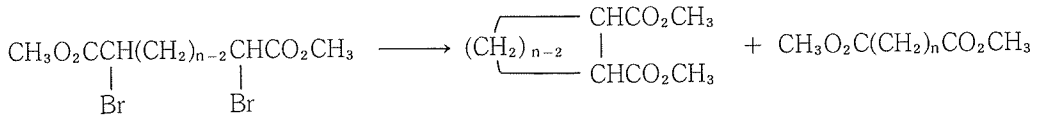
A mercury pool has often been used as a cathode to reduce a carbon-halogen bond.[1] The electrolysis of **1a** at a mercury cathode, however, gave **2a** in a lower yield and the product was accompanied by large amounts of open-chain esters **3a** and **4a** (Table 1, runs 7, 9). THF was found to give a higher yield of **2** than a more polar hexamethylphosphoramide (HMPA) or DMF although THF is not as good a solvent as HMPA or DMF in dissolving a supporting electrolyte (Table 1, runs 6 and 8, 11 and 13). When a mixed solvent of THF-HMPA or HMPA- acetonitrile was used, **2b** was obtained in a 9 to 13% yield. The electrochemical reaction of **1b** in dioxane did not occur and the starting material was recovered. Tetraalkylammonium perchlorate and tetraalkylammonium bromide were found to be effective as supporting electrolytes (Table 1, runs 10, 12). However, electrolysis of **1b** did not give the cyclized product **2b** when lithium chloride was used. A higher concentration of supporting electrolyte gave a higher yield of **2** (Table 1, runs 1, 2). The electrolysis with a lower concentration of **1** gave a higher yield of **2** as would generally be expected for the intramolecular reaction (Table 1, runs 5 and 6). Current density in the range of 10 to 25 mA/cm^2 did not appreciably affect the yields of cyclized product (Table 1, runs 3, 5).

Table 1. Results of electrolyses of dimethyl 2,4-dibromopentanedioate (**1a**) and dimethyl 2,5-dibromohexanedioate (**1b**) under various conditions[a]

Runs	Dibromide	Conc. of **1** (M)	Solv.	S. E.[b]	Conc. of S. E. (M)	c. d.[c] (mA/cm^2)	Electricity (F/mol)	Conv. of **1** (%)	Yield of **2** (%)[d]
1	**1a**	0.2	THF	TBAP	0.04	25	4	87	43
2	**1a**	0.2			0.1	25	4	84	57
3	**1a**	0.2			0.1	25	2	60	61
4	**1a**	0.2			0.1	25	1	38	59
5	**1a**	0.2			0.1	10	2	60	60
6	**1a**	0.1			0.1	10	2	66	74
7	**1a**	0.1			0.1	10[e]	2	97	18[f]
8	**1a**	0.1	DMF		0.1	10	2	63	20
9	**1a**	0.1			0.1	10[e]	2	86	11[g]
10	**1b**	0.2	THF		0.04	25	4	88	32
11	**1b**	0.2		TBAB	0.02	25	4	90	25
12	**1b**	0.2			0.04	25	4	86	30
13	**1b**	0.2	HMPA		0.02	25	4	77	17

a) Electrolyses were carried out at a constant current using platinum plate electrodes (2×2 cm^2). b) Supporting electrolyte : TBAP, tetrabutylammonium perchlorate ; TBAB tetrabutylammonium bromide. c) Current density. d) Yields based upon **1a** or **1b** consumed. e) Mercury pool was used as a cathode. f) Products **3a** (2%) and **4a** (19%) were also obtained. g) Products **3a** (1%) and **4a** (9%) were also obtained.

Cycloalkane **2** was obtained in a highest yield when a constant current electrolysis of **1** was conducted with 0.1M THF solution containing 0.1M tetrabutylammonium perchlorate at 10 mA/cm² by using a platinum cathode. Therefore, electrolyses of dimethyl 2, 4-dibromopentane- **(1a)**, dimethyl 2, 5-dibromohexane- **(1b)**, dimethyl 2, 6-dibromoheptane- **(1c)**, dimethyl 2, 7-dibromooctane- **(1d)** and dimethyl 2, 8-dibromononanedioate **(1e)** were carried out under these experimental conditions. The yields of dimethyl cycloalkane-1, 2-dicarboxylates **(2a-2e)** and the corresponding dimethyl alkanedioates **(3b-3e)** obtained from this electrolysis are summarized in Table 2.



1a, n=3 **c,** n=5 **e,** n=7

b, n=4 **d,** n=6

Scheme 5

Table 2. Yield of the products **2** and **3** in electrochemical reduction of **1**[a]

Dibromide	Conv. of **1** (%)	Yield of products (%)[b]	
		2	**3**
1a	66	74	0
1b	88	18	trace
1c	71	52	trace
1d	55	60	4
1e	54	20	12

a) Electrolysis of 0.1 M **1** in THF solution containing 0.1 M tetrabutylammonium perchlorate was carried out at 10 mA/cm² using platinum plate electrodes. Electricity passed was 2F per mol of **1**. b) Based on **1** consumed.

The ratio of *trans*- to *cis*-isomer was appreciably affected by the solvent, cathode material and electrolysis potential. The ratios of *trans* to *cis* isomer obtained under different conditions are shown in the last column in Table 3. The *trans* to *cis* ratio decreased when a platinum electrode was used as a cathode, or when THF was used as the solvent or when the electrolysis was carried out at a more negative potential. Since an electron transfer and the successive reactions occur on the surface of the electrode in the electrochemical reaction, it may be expected that the cathode material and electrolysis potential affect appreciably the stereochemical outcome of cyclized products. The *trans* and *cis* isomers were also separated from a mixture **2b** or **2c** obtained in the cyclization of dibromoalkanedioate **1b** or **1c**. Electrochemical cyclization of **1b** gave *trans*-**2b** almost exclusively, although dimethyl cyclobutane-1, 2-dicarboxylate prepared from diethyl malonate and dibromo ethane was found to be a mixture

Table 3. Yields of products **2a**, **3a** and **4a** and ratios of *trans* and *cis* isomers of **2a** in electrochemical reduction of **1a**[a]

Cathode	Potential (V *vs* S. C. E)	Solvent	Conv. of **1a** (%)	Yield of Products (%)[b]			*t*-**2a**/*c*-**2a**
				2a	**3a**	**4a**	
Pt	−[c]	THF	66	74	0	0	4
	−[c]	DMF	63	20	0	0	14
Hg	−[c]	THF	97	18	2	19	9
	−[c]	DMF	86	11	1	9	26
Hg	−0.5[d]	DMF	100	12	10	4	>40
	−0.5		59	14	trace	21	>40
	−0.6		98	18	2	16	35
	−0.7		100	28	6	0	27
	−0.9		100	28	8	0	27
	Zn powder[e]	aq. EtOH	100	13	13	0	18
	Zn-Cu[f]	DMF	100	28	trace	0	23

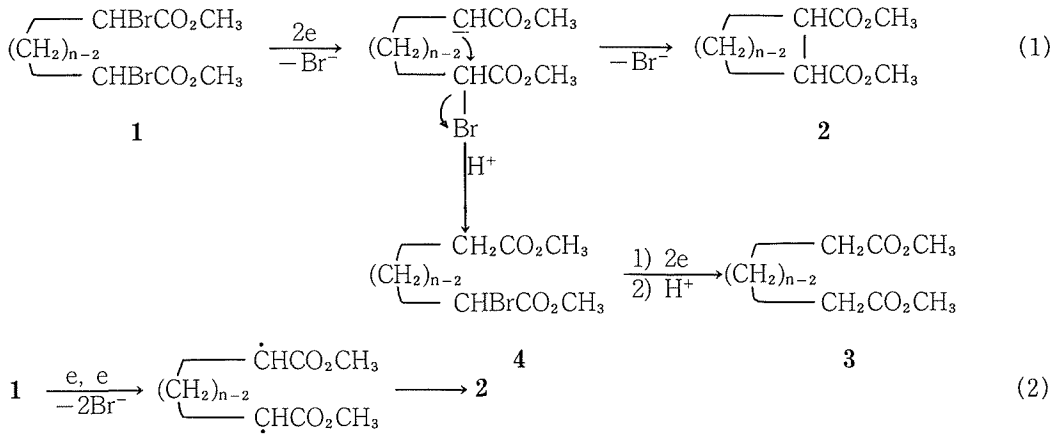
a) Electrolysis of 0.1 M **1a** was carried out in solutions containing 0.1 M Bu_4NClO_4. b) Based on **1a** consumed. c) Electrolysed at 10 mA/cm^2. d) Electrolysed using a divided cell. e) **1a** was reduced with zinc powder. f) **1a** was reduced with a zinc-copper couple.

of nearly equal amounts of *trans*- and *cis*-isomers. On the other hand, dimethyl cyclopentane-1, 2-dicarboxylate **2c** obtained by the electrolysis was a 6 : 4 mixture of *trans* and *cis* isomers. A more detailed investigation of this stereochemical outcome in this electrochemical cyclization is under investigation and will be reported later.

The current-potential curve in DMF solution at a mercury cathode showed that a reduction of **1a** starts at nearly −0.3 V *vs* S. C. E. Half-wave potential of ethyl 2-bromopropionate was reported to be −0.35 V *vs* S. C. E.[11c] Controlled potential electrolysis of **1a** was carried out at a mercury cathode in DMF solution, although most of the electrolyses in the present study were made at a platinum cathode in THF. The results are shown in Table 3. At more positive potentials such as −0.5 and −0.6 V, monobromo ester **4a** was formed predominantly. Even at −0.9, however, the yield of **2a** was not so high as that obtained by a constant current electrolysis using a platinum cathode.

Reduction of a carbon-halogen bond can also be achieved by the use of reagents such as zinc.[12] Thus, reduction of **1a** with zinc powder in aqueous ethanol[13] gave **2a** and **3a** in 13 and 13% yields and reduction of **1a** with a zinc-copper couple in DMF[14] gave only **2a** in 28% yield. These results show that the electrochemical method gives a higher yield of cyclized products than the chemical reduction.

There are at least two probable pathways by which the observed cyclized products are formed. In the first probable path, a two electron reduction of the carbon-bromine bonds of dimethyl 2,(ω−1) -dibromoalkanedioate **(1)** generates a stabilized carbanion which then undergoes an intramolecular nucleophilic attack on a carbon bearing bromine atom to end up at the observed cycloalkane **(2)** [Scheme 6 (1)]. In the second pathway the one electron reductions of two carbon-bromine bonds of dibromo diesters **(1)** may take place simultaneously to give a



Scheme 6

diradical. An intramolecular combination of this diradical would afford the observed product **(2)** [Scheme 6 (2)].

Of these two pathways, the diradical mechanism is less probable since it fails to explain the formation of monobromo ester **(4a)** and it would be rather difficult for the electron transfers at the two sites on the surface of the electrode to take place simultaneously. Moreover, the second electron transfer of the radical intermediate, if it is formed by one electron transfer, would be very fast and it would be immediately transformed into a carbanion. The results of a polarographic study of α-bromo esters, which showed one wave with a two-electron reduction,[11] also support the likelihood of the first path, involving two electron reduction.

3. Experimental Section

3.1 Solvent and Supporting Electrolyte

Hexamethylphosphoramide (HMPA), dried with calcium hydride, and tetrahydrofuran (THF), dried with lithium aluminum hydride, were distilled before use. Acetonitrile was dried over phoshorus pentoxide and distilled over sodium hydroxide. Dimethylformamide (DMF) and dioxane were distilled before use. Tetrabutylammonium bromide was prepared from tributylamine and butyl bromide and recrystallized from benzene. Tetrabutylammonium perchlorate was prepared from tetrabutylammonium bromide and perchloric acid and recrystallized from ethanol.

3. 2 Analysis

Products were isolated by distillation and by preparative g. l. p. c. with a JEOL JGC-20K instrument. IR spectra were obtained with a Hitachi EPI-22 spectrometer, and NMR spectra were measured with a Hitachi R-22 high-resolution spectrometer (90 MHz) using TMS as an internal reference. Mass spectra were obtained with a Hitachi RM-50GC mass spectrometer. Quantitative g. l. p. c. analyses were carried out with a Hitachi 063 instrument by an internal standard method.

3. 3 General Procedure for the Preparations of Dibromoalkanedioic Acid Esters (1)

Starting dibromo diesters **(1)** were prepared from the corresponding alkanedioic acid by the method of Shriner and Damschroder[15] and Vogel.[16] A mixture of alkanedioic acid (0.36 mol) and thionyl chloride (0.93 mol) was heated under reflux for 6 h. To this mixture was added phoshorus tribromide (1.0 ml) and then dry bromine (1.0 mol) in a dropwise manner at 65 to 70°C over a period of 15 h. The mixture was then refluxed for 20 h, by which time the evolution of hydrogen bromide had almost ceased. To this crude α, α' -dibromoalkanedioyl dichloride was added absolute methanol (2.5 mol) at 0°C and the mixture was refluxed for 10 h. After the reaction was completed, unreacted methanol and thionyl chloride were removed by distillation. The crude ester was dissolved in diethyl ether and the solution was washed with sodium hydrogensulfate solution, sodium carbonate solution and water successively, and then dried over magnesium sulfate. Distillation gave the corresponding dimethyl 2, (ω−1)- dibromoalkanedioate **(1)**, which was a mixture of *dl* and *meso* isomers, in a 70 to 90% yield. Some physical properties of **1a**–**1e** are recorded below.

Dimethyl 2, 4-dibromopentanedioate **(1a)** : bp 102–105°C/0.5 mmHg ; n_D^{25} 1.4975; IR (neat) 1740, 1430 cm^{-1} ; NMR (CCl_4) δ 2.67 (m, 2H), 3.81 (s, 6H), 4.40 ppm (m, 2H). Found : C, 26.54 ; H, 3.33 ; Br, 50.04%. Calcd for $C_7H_{10}O_4Br_2$: C, 26.44 ; H, 3.17 ; Br, 50.26%.

Dimethyl 2, 5-dibromohexanedioate **(1b)** : mp 72–74°C ; IR (CCl_4) 1750, 1440 cm^{-1} ; NMR (CCl_4) δ 2.15 (m, 4H), 3.80 (s, 6H), 4.22 ppm (m, 2H). Found : C, 28.67 ; H, 3.76 ; Br, 48.17%. Calcd for $C_8H_{12}O_4Br_2$: C, 28.94 ; H, 3.64 ; Br, 48.14%.

Dimethyl 2, 6-dibromoheptanedioate **(1c)** : bp 121–123°C/0.25 mmHg ; n_D^{22} 1.4922 ; IR (neat) 1740, 1730, 1430 cm^{-1} ; NMR (CCl_4) δ 1.55 (m, 2H), 2.05 (m, 4H), 3.78 (s, 6H), 4.17 ppm (t, 2H). Calcd for $C_9H_{14}O_4Br_2$: mol wt, 345.924. Found : mol wt, 345,923.

Dimethyl 2, 7-dibromooctanedioate **(1d)** : bp 125–128°C/3 mmHg ; n_D^{22} 1.4973 ; IR (neat) 1740, 1435 cm^{-1} ; NMR (CCl_4) δ 1.45 (m, 4H), 2.0 (m, 4H), 3.75 (s, 6H), 4.12 ppm (t, 2H). Found : C, 33.18 ; H, 4.44 ; Br, 44.33%. Calcd for $C_{10}H_{16}O_4Br_2$: C, 33.36 H, 4.48 ; Br, 44.39%.

Dimethyl 2, 8-dibromononanedioate **(1e)** : bp 150–153 °C/1 mmHg ; n_D^{20} 1.4972 ; IR (neat) 1740, 1435 cm^{-1} ; NMR (CCl_4) δ 1.42 (m, 6H), 2.0 (m, 4H), 3.77 (s, 6H), 4.14 ppm (t, 2H). Found : C, 35.37 ; H, 4.95 ; Br, 43.31%. Calcd for $C_{11}H_{18}O_4Br_2$: C, 35.32 ; H, 4.85 ; Br, 43.73%.

3. 4 Electrolysis

For most of the preparative electrolysis, a normal undivided cell (2.8 cm dia.) equipped with a magnetic stirrer, a reflux condenser, and a serum cap for the introduction of a nitrogen gas was used. Electrolysis was carried out under nitrogen atmosphere at a constant current with two platinum plate electrodes (2×2 cm^2). Controlled potential electrolysis was carried out with a Yanagimoto V8 potentiostat using a mercury pool (4.4 cm^2) as a cathode and a platinum plate (1×1 cm^2) as an anode. After electrolysis, the reaction mixture was dissolved in diethyl ether and the solution was washed with sodium thiosulfate solution and water, and dried over magnesium sulfate. Usual work-up of the solution gave a product mixture which was subjected to distillation and preparative g. l. p. c. with a JEOL-20K instrument to give pure products.

3. 5 Products from Electrolysis

Structures of new compounds were deduced by spectroscopy while the compounds described in the literature were identified by comparison with an authetic sample prepared by non-electrochemcial method. Some physical properties are recorded below.

trans-Dimethyl cyclopropane-1, 2-dicarboxylate (*t*-**2a**) : n_D^{25} 1.4408 ; IR (neat) 1740, 1720, 1020, 1430 cm^{-1} ; NMR (CCl_4) δ 1.27 (m, 2H), 2.00 (m, 2H), 3.60 ppm (s, 6H) ; MS *m/e* (rel intensity) 127 (M^+-OCH_3, 100), 126 (M^+-HOCH_3, 54), 99 ($M^+-CO_2CH_3$, 58), 98 ($M^+-HCO_2CH_3$, 92), 59 (53), 39 (55). Found : C, 53.11 : H, 6.53%. Calcd for $C_7H_{10}O_4$: C, 53.16 ; H, 6.37%.

cis-Dimethyl cyclopropane-1, 2-dicarboxylate (*c*-**2a**) : n_D^{25} 1.4455 ; IR (neat) 1740, 1720, 1430, 1020 cm^{-1} ; NMR (CCl_4) δ 1.09 (m, 1H), 1.53 (m, 1H), 1.87 (m, 2H), 3.57 ppm (s, 6H) ; MS *m/e* (rel intensity) 127 (100), 126 (18), 99 (34), 98 (40), 59 (31), 39 (34). Found : C, 52.96 ; H, 6.43%. Calcd for $C_7H_{10}O_4$: C, 53.16 ; H, 6.37%.

Dimethyl cyclobutane-1, 2-dicarboxylate (**2b**) : n_D^{21} 1.4459 ; IR (neat) 1740, 1730, 1440, 930, 900 cm^{-1} ; NMR (CCl_4) δ 2.21 (m,4H), 3.33 (m, 2H), 3.67 (s, 6H ; *t*-**2b**) or 3.64 ppm (s, 6H ; *c*-**2b**) ; MS of *trans*-**2b** *m/e* (rel intensity) 141 (M^+-OCH_3, 49), 140 (M^+-HOCH_3, 65), 113 ($M^+-CO_2CH_3$, 100), 112 ($M^+-HCO_2CH_3$, 69), 81 (41), 71 (49), 59 (59), 53 (41). MS of *cis*-**2b** *m/e* (rel intensity) 141 (65), 140 (48), 113 (100), 112 (24), 59 (43), 53 (35). Found : C, 55.98 ; H, 7.06%. Calcd for $C_8H_{12}O_4$: C, 55.80 ; H, 7.03%.

trans-Dimethyl cyclopentane-1, 2-dicarboxylate (*t*-**2c**) : n_D^{25} 1.4511 ; IR (neat) 1740, 1730, 1430 cm^{-1} ; NMR (CCl_4) δ 1.88 (m, 6H), 3.10 (m, 2H), 3.70 ppm (s, 6H) ; MS *m/e* (rel intensity) 155 (M^+-OCH_3, 34), 154 (M^+-HOCH_3, 29), 127 ($M^+-CO_2CH_3$, 24), 126 ($M^+-HCO_2CH_3$, 78), 67 (100), 59 (27). Found : C, 57.80 ; H, 7.44%. Calcd for $C_9H_{14}O_4$: C, 58.05 ; H, 7.58%.

cis-Dimethyl cyclopentane-1, 2-dicarboxylate (*c*-**2c**) : n_D^{25} 1.4550 ; IR (neat) 1740, 1730, 1425 cm^{-1} ; NMR (CCl_4) δ 1.95 (m, 6H), 2.96 (m, 2H), 3.62 ppm (s, 6H) ; MS *m/e* (rel intensity) 155 (40), 154 (29), 127 (11), 126 (43), 67 (100), 59 (27). Found : C, 57.08 ; H, 7.61%. Calcd for $C_9H_{14}O_4$: C, 58.05 ; H, 7.58%.

Dimethyl cyclohexane-1, 2-dicarboxylate (**2d**) : n_D^{23} 1.4525 ; IR (neat) 1735, 1730, 1430 cm^{-1} ; NMR (CCl_4) δ 1.45 (m, 4H), 1.9 (m, 4H), 2.65 (m, 2H), 3.64 ppm (s, 6H) ; MS *m/e* (rel intensity) 169 (M^+-OCH_3, 29), 168 (M^+-HOCH_3, 30), 141($M^+-CO_2CH_3$, 14),140 ($M^+-HCO_2CH_3$, 70), 81 (100), 59 (22). Found : C, 60.10 ; H, 7.98%. Calcd for $C_{10}H_{16}O_4$: C, 59.98 ; H, 8.05%.

Dimethyl cycloheptane-1, 2-dicarboxylate (**2e**) : n_D^{22} 1.4708 ; IR (neat) 1730, 1430 cm^{-1} ; NMR (CCl_4) δ 1.6 (m, 10H), 2.9 (m, 2H), 3.64 ppm (s, 6H) ; MS *m/e* (rel intensity) 183 (M^+-OCH_3, 32), 182 (M^+-HOCH_3, 40), 155 ($M^+-CO_2CH_3$, 13), 154 ($M^+-HCO_2CH_3$, 66), 95 (100), 59 (21). Calcd for $C_{10}H_{14}O_3$: *m/e* 182.094. Found : *m/e* 182.093.

Dimethyl pentanedioate (**3a**) : n_D^{25} 1.4220 ; IR (neat) 1730 cm^{-1} ; NMR (CCl_4) δ 1.86 (m, 2H), 2.25 (t, 4H), 3.57 ppm (s, 6H). Found : C, 52.39 ; H, 7.58%. Calcd for $C_7H_{12}O_4$: C, 52.49 ; H, 7.55%.

Dimethyl hexanedioate (**3b**) : n_D^{21} 1.4286 ; IR (neat) 1730 cm^{-1} ; NMR (CCl_4) δ 1.63 (m, 4H), 2.28 (m, 4H), 3.64 ppm (s, 6H). Found : C, 55.07 ; H, 8.03%. Calcd for $C_8H_{14}O_4$: C, 55.16 ; H, 8.10%.

Dimethyl heptanedioate (**3c**) : n_D^{25} 1.4287 ; IR (neat) 1735 cm^{-1} ; NMR (CCl_4) δ 1.55 (m, 6H),

2.26 (t, 4H), 3.67 ppm (s, 6H). Found : C, 57.41 ; H, 8.52%. Calcd for $C_9H_{16}O_4$: C, 57.43 ; H, 8.57%.

Dimethyl octanedioate (**3d**) : n_D^{21} 1.4339 ; IR (neat) 1735 cm^{-1} ; NMR (CCl_4) δ 1.5 (m, 8H), 2.25 (t, 4H), 3.62 ppm (s, 6H). Found : C, 59.31 ; H, 8.97%. Calcd for $C_{10}H_{18}O_4$: C, 59.38 ; H, 8.97%.

Dimethyl nonanedioate (**3e**) : n_D^{21} 1.4358 ; IR (neat) 1730 cm^{-1} ; NMR (CCl_4) δ 1.4 (m, 10H), 2.23 (t, 4H), 3.62 ppm (s, 6H). Found : C, 61.10 ; H, 9.47%. Calcd for $C_{11}H_{20}O_4$: C, 61.09 ; H, 9.32%.

3. 6 Synthesis of Dimethyl Cyclobutane-1, 2-dicarboxylate (2b)

An authentic sample of **2b** was prepared from diethyl malonate and dibromoethane by a modified method of Bailey and Sorenson.[17] Natrium (4.6 g, 0.2 mol) was dissolved in 100 ml of absolute ethanol. The solution was cooled and diethyl malonate (177 g, 1.1 mol) was added at once. This solution was stirred and heated under reflux while dibromoethane (18.8 g, 0.1 mol) was added dropwise over a 5 h period. After the reaction mixture was heated under reflux for an additional 30 h, ethanol was distilled off. To the concentrated residue was added 100 ml of water containing a few drops of sulfuric acid The aqueous layer was extracted with diethyl ether, and the extracts were combined with the original organic layer. The resulting solution was dried over magnesium sulfate, and diethyl ether was removed. Distillation of the residue gave diethyl malonate, diethyl cyclopropane-1, 1-dicarboxylate, and 7.8 g (23%) of tetraethyl butane-1, 1, 4, 4-tetracarboxylate, bp 203-216 °C/1.5 mmHg.

Natrium (1.2 g, 0.052 mol) was dissolved in 20 ml of absolute ethanol, and to the cooled solution was added dropwise tetraethyl butane-1, 1, 4, 4-tetracarboxylate (7.8 g, 0.023 mol). Bromine (10 g, 0.063 mol) was slowly added to this mixture, and the solution was stirred at room temperature for 1 h. After the ethanol was distilled off, the residue was washed several times with water. The aqueous solution was extracted with diethyl ether. Removal of the solvent gave a crude tetraethyl 1, 1, 2, 2-cyclobutanetetracarboxylate. To this crude ester was added concentrated sulfuric acid (8 ml), glacial acetic acid (8 ml), and water (25 ml). The mixture was heated under reflux for 4 h and the removal of water and ethyl acetate by distillation gave a crude cyclobutane-1, 2-dicarboxylic acid. The crude acid was esterified with methanol by the usual method. Distillation of the crude ester obtained gave a mixture of *trans*- and *cis*-dimethyl cyclobutane-1, 2-dicarboxylate (**2b**), bp 57-62 °C/3 mmHg.

3. 7 Reduction of Ia with Zinc or Zinc-Copper Couple

a) Bromoester **Ia** was reduced by the method of Slabey.[13] A mixture of zinc dust (0.65 g, 10 mmol), ethanol (2.5 ml), water (0.9 ml), sodium carbonate (0.5 g), and sodium iodide (0.1 g) was stirred under reflux while **Ia** (0.95 g, 3 mmol) in ethanol (2 ml) was added over a period of 3 h. After the mixture was heated under reflux for an additional 1 h, the solution was cooled and a precipitated white solid was filtered off. The mixture was extracted with pentane. G. l. p. c. analysis of the pentane extract showed the formation of **2a** (0.39 mmol, 13%) and **3a** (0.39 mmol, 13%).

b) Bromoester **1a** was reduced with a zinc-copper couple by the method of Corbin *et. al.*[14] Zinc dust (13 g) was washed three times with 3% hydrochloric acid (each 10 ml), six times with water (each 10 ml) and four times with 2% copper (II) sulfate solution until the blue color disappeared. The resulting zink-copper couple was further washed with water, acetone and diethyl ether successively, and dried over phosphorus pentoxide. To a mixture of zinc-copper couple (10 mmol) and DMF (5 ml) was added **1a** (1.0 g, 3.2 mmol) in DMF (1 ml) over a period of 15 minutes. The resulting mixture was stirred overnight at room temperature and treated as described for zinc reduction. G. l. p. c. analysis of the reaction mixture showed the formation of **2a** (0.90 mmol, 28%) and a trace of **3a**.

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