

Electrochemical Reductive Cyclisation of Dimethyl 2,($\omega - 1$)-Dibromoalkanedioates

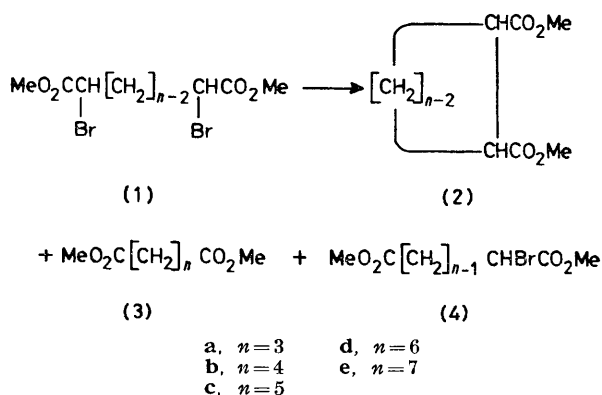
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Summary Electrochemical reduction of dimethyl 2,($\omega - 1$)-dibromoalkanedioates (**1**) in tetrahydrofuran solution containing tetra-*n*-butylammonium perchlorate using a platinum cathode produces the corresponding dimethyl cycloalkane-1,2-dicarboxylates (**2**).

ELECTROCHEMICAL reduction of 1,3-dihalides, which takes place readily to give cyclopropanes in good yields,¹⁻³ is a useful procedure for the preparations of substituted and strained cyclopropanes.¹⁻³ Cyclobutane has been prepared from 1,4-dibromobutane but in a lower yield,¹ whereas higher cycloalkanes have not yet been produced by such an electrochemical reduction. We report here that electrochemical reduction of 1, ω -dibromides containing alkoxy-carbonyl groups at both termini produced three- to seven-membered ring cycloalkanes in moderate yields. This electrochemical reaction provides a convenient means of synthesis of cycloalkane-1,2-dicarboxylic acid esters, not readily prepared otherwise.

Constant-current electrolysis of the dibromoalkanedioates (**1**)[†] in tetrahydrofuran (THF) solution containing tetra-*n*-butylammonium perchlorate (0.1 M) as supporting electrolyte produced the corresponding cycloalkanedicarboxylates (**2**) as the main product. Reactions were



conveniently carried out in a normal undivided cell with two platinum plate electrodes. Results for the reduction of (**1**) are in the Table.

TABLE. Electrochemical reduction of (**1**)^a

Substrate	[(1)]/ mol l ⁻¹	Current density /A cm ⁻²	Recovered (1)/%	Yield/% ^b	
				(2)	(3)
(1a)	0.2	0.025	40	61	—
"	0.2	0.01	40	60	—
"	0.1	0.01	34	74	—
(1b)	0.2 ^c	0.025 ^d	12	32	—
"	0.1	0.01	32	18	Trace
(1c)	0.1	0.01	29	52	Trace
(1d)	0.1	0.01	45	60	4
(1e)	0.1	0.01	46	20	12

^a Electrolysis in THF solution containing 0.1 M-Bu₄NClO₄ with platinum plate electrodes. 2 F mol⁻¹ of electricity passed.

^b Based on (**1**) consumed. Compounds (**2**) and (**3**) gave satisfactory analytical results and had the expected spectral data.

^c Electrolysed in THF solution containing 0.04 M-Bu₄NClO₄.

^d 4 F mol⁻¹ of electricity passed.

The highest yields of (**2a**) were obtained with low concentration of (**1a**) using a platinum plate cathode in THF solution. Dimethylformamide (DMF) or hexamethylphosphoramide (HMPA) were not effective as solvents for the preparation of (**2**). Tetra-*n*-butylammonium bromide could also be used as supporting electrolyte. Use of a mercury pool cathode led to a sharp decrease in the yield of (**2a**) and to the formation of the alkanedioates (**3**) and (**4**). The decreased yields of (**2**) are probably due to the formation of organomercurials,⁴ although they were not isolated in our experiments. Constant-current electrolyses of the alkanedioates (**1b**)—(**1e**) in THF solution containing Bu₄NClO₄ using a platinum cathode also produced the cycloalkanedicarboxylates (**2b**)—(**2e**) (Table); the α -bromoesters (**4**) were not detected.

Reductive cyclisation was also carried out with a zinc-copper couple⁵ or zinc powder.⁶ Treatment of (**1a**) in DMF with zinc-copper couple produced (**2a**) in 28% yield, whereas treatment with zinc powder in aqueous ethanol

[†] The dibromoalkanedioates (**1**) were conveniently prepared from the corresponding alkanedioic acid chlorides and bromine using phosphorus tribromide (A. Vogel, *J. Chem. Soc.*, 1948, 648).

produced (**2a**) and (**3a**), both in 13% yield. These results show that the electrochemical method is better for reductive cyclisations.

Although the detailed mechanism of these electrochemical reactions is not clear at present, the following stereochemical aspects should be noted. Distillation and preparative g.l.c. of the electrolysed mixture of (**1a**) gave *trans*-(**2a**) [n_D^{25} 1.4408 (lit.,⁷ n_D^{24} 1.4418); δ (CCl₄) 1.27 (m, 2H), 2.00 (m, 2H), and 3.60 (s, 6H) (identical to that in ref. 8); *m/e* 127 (100%), 126 (54), 99 (58), 98 (92), and 59 (53)] and *cis*-(**2a**) [n_D^{25} 1.4455 (lit.,⁷ n_D^{24} 1.4438); δ 1.09 (m, 1H), 1.53 (m, 1H), 1.87 (m, 2H), and 3.57 (s, 6H); *m/e* 127 (100%),

126 (18), 99 (34), 98 (40), and 59 (31)], and, as shown by g.l.c. analysis (Carbowax 20M, 15%), the ratio of the *trans*- to *cis*-isomers was affected considerably by the solvent, cathode material, and electrolysis potential. For example, electrolysis of (**1a**) in THF and in DMF using a platinum cathode produced (**2a**) with *trans* to *cis* ratios of 4:1 and 15:1, respectively. With a mercury cathode, the corresponding ratios were 9:1 and 26:1, respectively, and ratios of ca. 20:1 were obtained when the reductive cyclisation was carried out with the zinc-copper couple or zinc powder.

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