

ELECTROCHEMICAL CYCLIZATION OF TETRAMETHYL ESTERS OF 2-SUBSTITUTED  
PROPANE-1,1,3,3-TETRACARBOXYLIC ACIDS IN THE PRESENCE OF SALTS  
OF HYDROHALIC ACIDS

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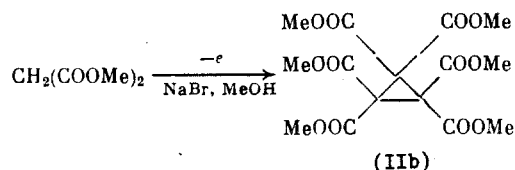
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The chemical and electrochemical cyclization of tetramethyl esters of 2-substituted propane-1,1,3,3-tetracarboxylic acids in the presence of hydrohalic acid salt mediators were studied. It was found that the chemical variant of the cyclization of the corresponding  $\alpha, \alpha'$ -dianions of esters of propane-1,1,3,3-tetracarboxylic acids by the action of iodine or bromine is substantially inferior to the electrochemical variant. In the latter case, the esters of substituted cyclopropane-1,1,2,2-tetracarboxylic acids are formed in a 87-98% yield. The tetramethyl ester of 2-isopropylpropane-1,1,3,3-tetracarboxylic acid, which under the electrolysis conditions decomposes according to a Michael retroreaction is an exception.

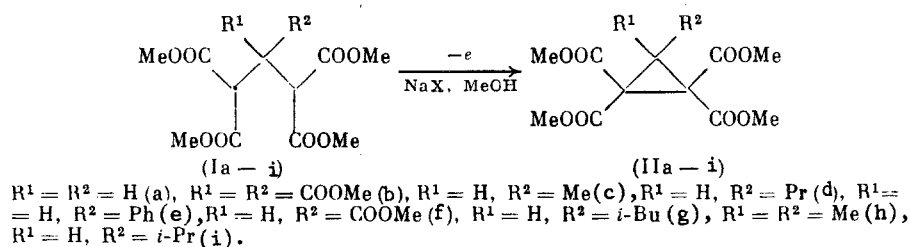
$\alpha, \alpha'$ -Dianions of 2-substituted esters of propane-1,1,3,3-tetracarboxylic acids cyclize by the action of iodine or bromine into esters of cyclopropanecarboxylic acids [1, 2], but the yield of the reaction products was not reported.

It was also found that during electrolysis in the presence of NaI, the tetramethyl ester of propane-1,1,3,3-tetracarboxylic acid (Ia) cyclizes into the tetramethyl ester of cyclopropane-1,1,2,2-tetracarboxylic acid (IIa), but the cyclization of the hexamethyl ester of propane-1,1,2,2,3,3-hexacarboxylic acid (Ib) could not be effected [3].

The electrochemical cyclization of 2-substituted esters of propane-1,1,3,3-tetracarboxylic acids was carried out by us for the first time [4]. This made it possible to obtain subsequently the cyclic hexaester (IIb) in one step by electrochemical oxidation directly from malonic ester [5]



In the present work, we undertook a more detailed investigation of the electrochemical cyclization of esters of 2-substituted propane-1,1,3,3-tetracarboxylic acids (Ia-i) in the presence of electron transfer catalysts (ETC) using hydrohalic acid salts as such (Table 1).



The cyclization of esters (Ib-i) was carried out in the presence of 0.5 equiv. of NaI at 30°C in a MeOH solution under conditions defined previously as optimal for the electrochemical cyclization of (Ia) [6].

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TABLE 1. Electrochemical Cyclization of  $(\text{MeOOC})_2\text{CHCR}^1\text{R}^2\text{CH}(\text{COOMe})_2$  (Ia-i) in Methanol in the Presence of NaI<sup>a</sup>

Experi- ment No.	R <sup>1</sup>	R <sup>2</sup>	Starting compound	Conver- sion, %	Current effi- ciency of (II) or product yield based on (I) used, %	Product yield of (II), based on converted (I), %	Other reaction products, product yield, based on converted (I), %
1	H	H	(Ia)	100	98	98	(MeOOC) <sub>2</sub> CHC(OMe)(COOMe) <sub>2</sub> (III), 12
2	COOMe	COOMe	(Ib)	30	26	87	(III), 18; (MeOOC) <sub>2</sub> C=C(COOMe) <sub>2</sub> (IV), 6
3 <sup>b</sup>	COOMe	COOMe	(Ib)	24	46	66	—
4	Me	H	(Ic)	100	95	95	—
5	n-Pr	H	(Id)	90	88	98	—
6	Ph	H	(Ie)	95	90	95	—
7 <sup>b</sup>	Ph	H	(Ie)	75	62	83	—
8 <sup>c</sup>	Ph	H	(Ie)	70	67	96	—
9	COOMe	H	(If)	98	96	97	—
10	i-Bu	H	(Ig)	68	65	96	Me <sub>2</sub> C=C(COOMe) <sub>2</sub> (V), 3
11	Me	Me	(Ih)	62	58	94	(V), 3
12 <sup>d</sup>	Me	Me	(Ih)	100	45	90	i-PrCH=C(COOMe) <sub>2</sub> (VI), 35; i-PrC(OMe)CH(COOMe) <sub>2</sub> (VII), 32; (III), 30; (Ib), 10; C(OMe) <sub>2</sub> (COOMe) <sub>2</sub> (VIII), 15
13	i-Pr	H	(Ii)	75	—	—	(VI), 40; (VII), 31; (Ib), 23; (III), 15; (VIII), 18
14 <sup>b</sup>	i-Pr	H	(Ii)	74	—	—	(VI), 36; (VII), 32; (Ib), 18; (III), 22; (VIII), 16
15 <sup>e</sup>	i-Pr	H	(Ii)	74	—	—	—

<sup>a</sup>8 mmoles of ester (I), 4 mmoles of NaI in 20 ml of MeOH, Fe-cathode, Pt-anode, 2F of electricity consumed per 1 mole of ester (I) at 30°C, current density 220 mA/cm<sup>2</sup>, temperature fluctuations during the electrolysis  $\pm 2^\circ\text{C}$ .

<sup>b</sup>Chemical oxidation of  $\alpha, \alpha'$ -dianion of (I) by 1 equivalent of I<sub>2</sub> in methanol at 30°C.

<sup>c</sup>Electrochemical cyclization in a MeOH-MeCN mixture (3:1).

<sup>d</sup>5.5F of electricity consumed per 1 mole of (Ih).

<sup>e</sup>Electrolysis in the presence of 4 mmoles of NaBr.

TABLE 2. Electrochemical Cyclization of  $(\text{MeOOC})_2\text{CHC}(\text{COOMe})_2 \cdot \text{CH}(\text{COOMe})_2$  (Ib) in Methanol in the presence of NaBr<sup>a</sup>

Ex- peri- ment No.	T, °C	Con- ver- sion of (Ib), %	Current effi- ciency of (IIb), and/or product yield based on (Ib) used, %	Product yield of (IIb) based on converted (Ib), %	Other reaction products, product based on converted (Ib), %
1	60	44	23	52	(III), 17; (IV), 23
2	50	61	42	69	(III), 10; (IV), 17
3	40	57	43	75	(III), 7; (IV), 11
4	30	53	46	87	(III), 6; (MeOOC) <sub>2</sub> C(OMe)CBr(COOMe) <sub>2</sub> (IX), 5
5 <sup>b</sup>	30	45	34	76	(III), 12; (IV), 11
6 <sup>c</sup>	30	98	34/83	85	(III), 5; (X), 2
7	20	40	24	60	(III), 5; (MeOOC) <sub>2</sub> CBrC(COOMe) <sub>2</sub> CH(COOMe) <sub>2</sub> (X), 32

<sup>a</sup>8 mmoles of ester (Ib), 4 mmoles of NaBr in 20 ml of MeOH, Fe cathode, Pt anode, 2F of electricity consumed per 1 mole of ester (Ib), current density 220 mA/cm<sup>2</sup>, temperature fluctuations during electrolysis  $\pm 2^\circ\text{C}$ .

<sup>b</sup>Chemical oxidation of  $\alpha, \alpha'$ -dianion of (Ib) with 1 equivalent of Br<sub>2</sub> in methanol.

<sup>c</sup>5F of electricity consumed per mole of ester (Ib).

Under these conditions the monosubstituted derivatives of (Ia) — esters (Ic-f) containing unbranched alkyl groups or planar Ph and COOMe substituents — cyclize with 88-95% current efficiency. It was found that even the isobutyl group (Ig) creates considerable steric hindrances for the electrocyclization, which are comparable to the effect of substitution of two central H atoms in (Ia) by two Me groups, whereby the current efficiency decreases to 60-70%.

Still greater steric hindrances for the electrochemical cyclization are produced by two additional central COOMe groups in (Ib), where the current efficiency is 26%. However, in all cases where the electrochemical cyclization is carried out, it proceeds in a high product yield based on the converted (I) — 87-98%, and thus a high yield of the cyclization product (II) can be attained by consuming a large amount of electricity (see, for example, experiment 12, Table 1).

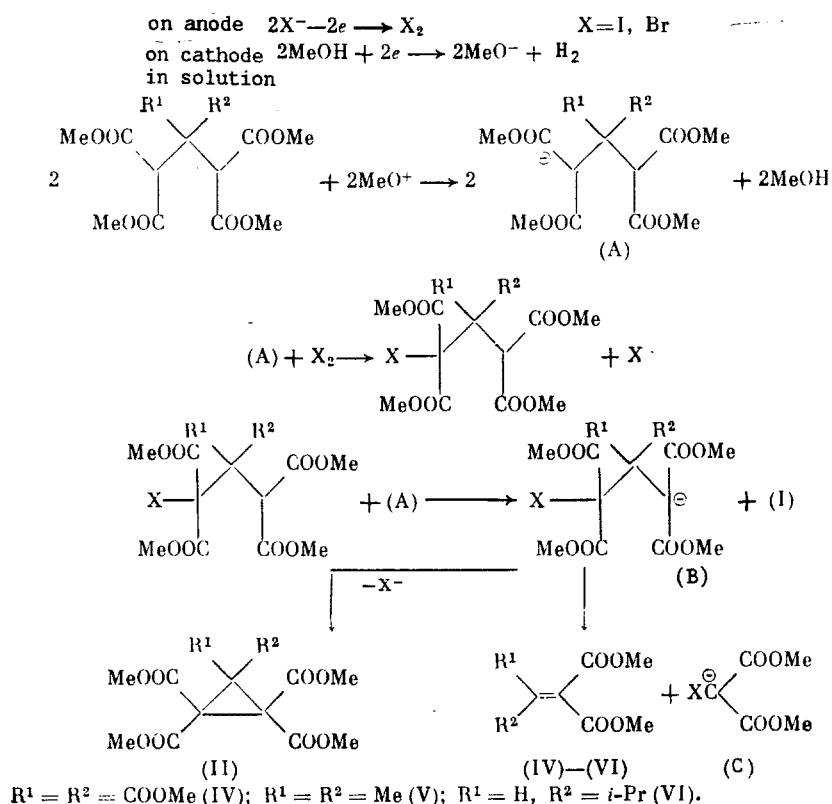
Since no quantitative characteristics of the chemical cyclization of (I) were previously reported, we also carried out a chemical cyclization of  $\alpha, \alpha'$ -dianions of (Ib, e) by the action of 1 equiv. of I<sub>2</sub> (experiments 3, 7, Table 1). Comparison with similar data for the electrochemical cyclization (experiments 2, 6) indicate the superiority of the electrochemical method. It was found previously that the electrocyclization of (Ia) in MeCN proceeds much more poorly than in MeOH [6]. The electrocyclization of (Ib, e) in MeCN generally does not occur. When 2F of electricity were consumed per 1 mole of (Ib, e) in MeCN in the presence of 0.5 equiv. of NaI, the conversion of (Ib, e) did not exceed 5-10%.

Moreover, the electrocyclization of (Ie) was substantially complicated even when the reaction was carried out in a MeOH/MeCN mixture (3:1) (experiment 8, Table 1).

Compound (Ii) containing the i-Pr group could not be cyclized by the electrochemical method. A cyclic product also was not obtained during the oxidation of the  $\alpha, \alpha'$ -dianion of (Ii) by bromine or iodine. The low current efficiency of (IIb) could be increased from 26 to 46% when NaBr was used as the ETC (Table 2). As in the case when NaI was used, the temperature of 30°C was found to be optimal for the cyclization. In acetonitrile in the presence of NaBr, compound (Ib) does not undergo cyclization and likewise in the presence of NaI.

The chemical variant — cyclization of the  $\alpha, \alpha'$ -dianion of (Ib) by the action of Br<sub>2</sub> (experiment 7, Table 2) is also markedly inferior to the electrochemical method. When 5F of electricity were consumed per mole of (Ib) at 30°C in the presence of NaBr, compound (IIb) was obtained in an 85% product yield. When the temperature of the electrochemical cyclization was lowered to 20°C, the hexamethyl ester of 1-bromopropane-1,1,2,2,3,3-hexacarboxylic acid, which is not convertible to (IIb) under these conditions, was also obtained in considerable amounts.

The data obtained, and also the results obtained in [3, 7, 8] make it possible to suggest the following reaction mechanism:



When the process is carried out in acetonitrile, anion (A) practically does not form, either as the result of the cathode reduction or by the reaction of (Ib, e) with metallic sodium generated on the surface of the cathode. As a result the process has a cyclic form with the formation of Na on the cathode and  $I_2$  on the anode, with subsequent regeneration of NaI during their interaction; thus, compounds (Ib, e) practically do not convert (the conversion does not exceed 5-10%). Decrease in the current efficiency of (IIe) on carrying out the reaction in the MeOH-MeCN mixtures is possibly explained by the lower solubility of the intermediate anion (A) in this mixture of solvents.

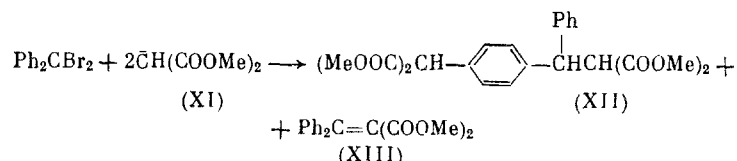
The main side reaction is the dissociation of the intermediate anion (B) according to the Michael retro-reaction. The formation of unsaturated esters (IV)-VI was recorded in several cases (Tables 1, 2). The addition of MeOH to (IV) and (VI) under the electrolysis conditions leads to methoxy-substituted (III) and (VII), respectively. The extraordinarily reactive anion (C) is capable, as a result of chemical as well as electrochemical transformations, to form a broad spectrum of compounds, such as for example (IIb), (III), (IV), (VIII), and (IX).

The dissociation of anion (A) by the Michael retro-reaction became the main reaction during the electrooxidation of (Ii). This conclusion borne out by the formation of a cyclic compound (IIi) in a 95% yield by the action of MeONa on the tetramethyl ester of 1-bromo-2-isopropylpropane-1,1,3,3-tetracarboxylic acid.

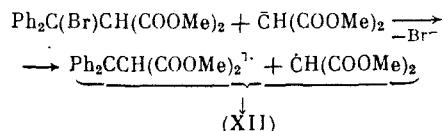
The considerable influence of steric hindrances during the intermolecular alkylation of malonic ester anions by alkylhalide has been observed many times before [3, 7]. In the case of (Ii), the steric screening of anion (A) is possibly sufficient to prohibit the intermolecular interaction of the latter with  $Br_2$  and  $I_2$ . As a result a competing dissociation of anion (A) is realized by the Michael retro-reaction.

For a more complete clarification of the influence of substituents on the cyclization of 2,2-disubstituted ester of propane-1,1,3,3-tetracarboxylic acid, we tried to synthesize the previously described [9] tetramethyl ester of 2,2-diphenylpropane-1,1,3,3-tetracarboxylic acid (Ij,  $R^1 = R^2 = Ph$ ). However in the reaction of dibromo-

diphenylmethane with sodium-malonic ester (XI), we obtained only the tetramethyl ester (XII) isomeric with (Ij) in a 65% yield, together with unsaturated ester (XIII) in 26% yield



Since the  $\text{pK}_a$  of diphenylmethane exceeds the  $\text{pK}_a$  of malonic ester by more than 16 units [10], the ionic  $\text{Br}_t^+$  mechanism is not very probable [11]. It is clear that the reaction of (XIV) with the second molecule of (XI) proceeds by a one-electron transfer mechanism



## EXPERIMENTAL

The GLC analysis was carried out on an LKhM-8MD chromatograph with a flame ionization detector in a  $\text{N}_2$  current, using stainless steel columns: 1)  $3000 \times 3$  mm with 10% FFAP on a Celite 545 (60-80 mesh), 2)  $1000 \times 3$  mm with 3% OV-225 on Chromaton N-super (0.125-0.16 mm). The NMR spectra of the organic compounds in  $\text{CDCl}_3$  were recorded on "Tesla BS-60" (60 MHz) and "Bruker M-250" (250 MHz) spectrometers, using TMS as internal standard. The analytically pure grade NaI and NaBr reagents were additionally dried in vacuo.

The tetramethyl esters (Ia, c-g, i) were obtained by condensation of malonic ester with the corresponding aldehyde: (Ib) was synthesized by the method described in [8]. Compounds (V) and (VI) were obtained by the condensation of acetone and isobutanal, respectively, with malonic ester. Compound (Ih) was synthesized by addition of malonic ester to (V). Dibromodiphenylmethane was obtained by bromination of diphenylmethane with N-bromosuccinimide.

Electrochemical Oxidation of Tetraesters (Ia-i). General Procedure. An 8 mmoles portion of the ester of (I), 4 mmoles of electrolyte (ETC), and 20 ml of solvent were placed in a diaphragmless cell with a Pt anode, Fe cathode (distance between the electrodes-5 mm), with external cooling, and equipped with a magnetic stirrer, a cooler, and thermometer; the electrolysis was carried out at a current density of  $220 \text{ mA/cm}^2$  by passing an amount of electricity indicated in Tables 1 and 2. The reaction mixture was evaporated, the residue was extracted with chloroform, the extract was washed with water, and dried over  $\text{MgSO}_4$ . Chloroform was evaporated and the residue was subjected to a quantitative PMR analysis, using 1,4-dichlorobenzene or t-BuOH as internal standard. In several cases, the yield of (II) was also determined by the GLC method.

The  $\alpha, \alpha'$ -dianions of (I) were obtained by mixing (I) with 2 equiv. of MeONa in MeOH. The oxidation with iodine and bromine was carried out on a scale of an electrochemical experiment. Compounds (IIa, b, e, h) were previously described in [4].

Tetramethyl ester of 3-methylcyclopropane-1,1,2,2-tetracarboxylic acid (IIc) was isolated in a 95% yield from experiment 4 (Table 1), bp  $126-128^\circ\text{C}$  (0.04 mm), mp  $51-53^\circ\text{C}$ . Found: C 50.22; H 5.67%.  $\text{C}_{12}\text{H}_{16}\text{O}_8$ . Calculated: C 50.00; H 5.56%. PMR spectrum ( $\delta$ , ppm): 139 d (3H,  $\text{CH}_3$ ), 2.46 q (1H, CH), 3.71 s and 3.72 s (12H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR spectrum ( $\delta$ , ppm): 8.3 q ( $\text{CH}_3$ ), 31.4 d (CH), 43.9 s (C), 52.7 q and 53.1 q ( $\text{OCH}_3$ ), 165.0 s and 167.0 s ( $\text{C}=\text{O}$ ).

Tetramethyl ester of 3-propylcyclopropane-1,1,2,2-tetracarboxylic acid (IIId) was isolated in a 80% yield from experiment 5 (Table 1), bp  $130-132^\circ\text{C}$  (0.06 mm), mp  $66-68^\circ\text{C}$ . Found: C 53.40; H 6.39%.  $\text{C}_{14}\text{H}_{20}\text{O}_8$ . Calculated: C 53.16; H 6.33%. PMR spectrum ( $\delta$ , ppm): 0.93 t (3H,  $\text{CH}_3$ ), 1.44 m (2H,  $\text{CH}_2$ ), 1.78 q (2H,  $\text{CH}_2$ ), 2.38 t (1H, CH), 3.74 s and 3.75 s (12H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR spectrum ( $\delta$ , ppm): 13.3 q ( $\text{CH}_3$ ), 21.9 t ( $\text{CH}_2$ ), 24.9 t ( $\text{CH}_2$ ), 36.7 d (CH), 43.7 s (C), 52.6 q and 53.0 q ( $\text{OCH}_3$ ), 165.0 and 167.0 s ( $\text{C}=\text{O}$ ).

Pentamethyl ester of cyclopropane-1,1,2,2,3-pentacarboxylic acid (IIIf) was isolated in a 92% yield from experiment 9 (Table 1), mp  $117-118^\circ\text{C}$ . Found: C 47.23; H 4.94%.  $\text{C}_{13}\text{H}_{16}\text{O}_{10}$ . Calculated: C 46.99; H 4.82%. PMR spectrum ( $\delta$ , ppm): 3.18 s (1H, CH). 3.81 s (9H,  $\text{OCH}_3$ ), 3.85 s (6H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR spectrum ( $\delta$ , ppm): 33.8 d (CH), 43.0 s (C), 52.7 q, 53.2 q and 53.4 q ( $\text{OCH}_3$ ), 163.5 s, 164.9 s and 165.0 s ( $\text{C}=\text{O}$ ).

Tetramethyl ester of 3-isobutylcyclopropane-1,1,2,2-tetracarboxylic acid (IIg) was isolated in a 80% yield after additional passing of 1F of electricity through the reaction mixture (experiment 10, Table 1), bp 131-132°C (0.05 mm). Found: C 53.83; H 6.78%.  $C_{15}H_{22}O_8$ . Calculated: C 54.54; H 6.67%. PMR spectrum ( $\delta$ , ppm): 0.87 d (6H,  $CH_3$ ), 1.52-1.69 m (3H,  $CH-CH_2$ ), 2.32 t (1H, ring CH), 3.67 s (12H,  $OCH_3$ ).  $^{13}C$  NMR spectrum ( $\delta$ , ppm): 21.9 q ( $CH_3$ ), 28.1 d (CH), 31.2 t ( $CH_2$ ), 35.8 d (CH), 43.6 s (C), 52.6 and 53.1 q ( $OCH_3$ ), 165.1 s and 167.1 s ( $C=O$ ).

Tetramethyl ester of 3-isopropylcyclopropane-1,1,2,2-tetracarboxylic acid (IIIi) was obtained by cyclization of tetramethyl ester of 1-bromo-2-isopropylpropane-1,1,3,3-tetracarboxylic acid by the action of MeONa, and was isolated in a yield of 88%, bp 120°C (0.03 mm),  $n_D^{25}$  1.4565. Found: C 53.28; H 6.43%.  $C_{14}H_{20}O_8$ . Calculated: C 53.16; H 6.33%. PMR spectrum\* ( $C_6D_6$ ,  $\delta$ , ppm): 1.19 d ( $CH_3$ ,  $H^1$ ,  $J_{1,2} = 6.6$ ,  $J_{1,3} = -0.4$  Hz), 2.50 m (CH in i-Pr,  $H^2$ ,  $J_{2,3} = 10.8$  Hz), 2.55 d.d (ring CH,  $H^3$ ), 3.49 s and 3.52 s (12H,  $OCH_3$ ).  $^{13}C$  NMR spectrum ( $\delta$ , ppm): 21.7 q ( $CH_3$ ), 23.4 d (CH), 43.9 s (C), 44.2 d (CH), 52.7 q and 53.1 q ( $OCH_3$ ), 165.1 s and 167.0 s ( $C=O$ ).

The preparation and properties of compounds (III), (IV) and (VIII) were previously described in [7, 8].

Dimethyl ester of 3-methyl-3-methoxybutane-1,1-dicarboxylic acid (VII) was obtained electrochemically by addition of methanol to (VI) on the background of NaI, bp 56°C (0.04 mm),  $n_D^{23}$  1.4328. Found: C 54.88; H 8.31%.  $C_{10}H_{18}O_5$ . Calculated: C 55.04; H 8.26%. PMR spectrum ( $C_6D_6$ ,  $\delta$ , ppm): 0.89 d (6H,  $CH_3$ ), 1.84 m (1H, CH), 3.26 s, 3.32 s and 3.34 s (9H,  $OCH_3$ ), 3.79 d (1H, CH,  $J_1 = 8.5$  Hz), 3.91 d.d (1H, OCH,  $J_2 = 3.5$  Hz).  $^{13}C$  NMR spectrum ( $\delta$ , ppm): 16.2 q, 19.5 q ( $CH_3$ ), 31.2 d (CH), 52.2 q, 52.3 q and 55.4 q ( $OCH_3$ ), 60.9 d (CH), 84.3 d (OCH), 167.9 s and 168.1 s ( $C=O$ ).

When a base-catalyzed addition of MeOH to (VI) was attempted, the latter isomerized rapidly into the dimethyl ester of 3-methylbut-2-ene-1,1-dicarboxylic acid. PMR spectrum ( $\delta$ , ppm): 1.63 s and 1.73 s (6H,  $CH_3$ ), 3.68 s (6H,  $OCH_3$ ), 4.21 d (1H, CH), 5.39 d (1H,  $CH=$ ).  $^{13}C$  NMR spectrum ( $\delta$ , ppm): 21.5 q and 25.4 q ( $CH_3$ ), 51.1 d (CH), 52.2 q ( $OCH_3$ ), 115.8 d ( $CH=$ ), 137.9 s ( $C=$ ), 168.7 s ( $C=O$ ).

Hexamethyl ester of 1-bromopropane-1,1,2,2,3,3-hexacarboxylic acid (X) was isolated by fractional crystallization of the precipitate (experiment 7, Table 1) from methyl ethyl ketone, mp 179-180°C. Found: C 38.45; H 4.01; Br 16.91%.  $C_{15}H_{19}O_{12}Br$ . Calculated: C 38.22; H 4.03; Br 16.98%. PMR spectrum ( $\delta$ , ppm): 3.74 s, 3.82 s and 3.84 s (18H,  $OCH_3$ ), 5.24 s (1H, CH).  $^{13}C$  NMR spectrum ( $\delta$ , ppm): 53.1 q, 53.4 q, 54.4 q ( $OCH_3$ ), 53.7 d (CH), 62.2 s (C), 64.8 s (C-Br), 166.6 s, 169.9 s ( $C=O$ ).

Dimethyl ester of 2-[4-(dicarbomethoxymethyl)phenyl]-2-phenylethane-1,1-dicarboxylic acid (XII), mp 156-157°C (acetone). Found: C 64.87; H 5.68%.  $C_{23}H_{24}O_6$ . Calculated: C 64.49; H 5.61%. PMR spectrum ( $\delta$ , ppm): 3.54 s and 3.56 s (6H,  $OCH_3$ ), 3.73 s (6H,  $OCH_3$ ), 4.35 d (1H, CH,  $J = 12$  Hz), 4.58 s (1H, CH), 4.78 d (1H, CH,  $J = 12$  Hz), 7.15-7.40 m (9H,  $C_6H_5$  and  $C_6H_4$ ).  $^{13}C$  NMR spectrum ( $\delta$ , ppm): 50.7 d (CH), 52.6 q and 52.8 q ( $OCH_3$ ), 57.0 d (2CH), 127.0 d, 127.8 d, 128.0 d, 129.5 d, 131.1 s, 140.8 s, 141.3 s ( $C_6H_5$  and  $C_6H_4$ ), 167.7 s, 167.8 s, 168.2 s ( $C=O$ ).

Dimethyl ester of 2,2-diphenylethylene-1,1-dicarboxylic acid (XIII), mp 122-123°C (ether). Found: C 72.97; H 5.56%.  $C_{18}H_{16}O_4$ . Calculated: C 72.97; H 5.41%. PMR spectrum ( $\delta$ , ppm): 3.61 s (6H,  $OCH_3$ ), 7.16-7.40 m (10H,  $C_6H_5$ ).

Tetramethyl ester of 1-bromo-2-isopropylpropane-1,1,3,3-tetracarboxylic acid (XIV) was obtained by the action of 1.2 equiv. of N-bromosuccinimide on (II) in  $CCl_4$  solution. The unreacted (II) was separated by fractional crystallization from pentane. Compound (XIV) was isolated from the mother liquor in the form of a colorless viscous oil, yield 50%. PMR spectrum ( $\delta$ , ppm): 0.93 d and 0.97 d (6H,  $CH_3$ ), 2.1 m (1H, CH in i-Pr), 3.44 t (1H,  $C^2H$ ), 3.69 s, 3.73 s and 3.76 s (12H,  $OCH_3$ ), 3.89 d (1H,  $C^3H$ ).  $^{13}C$  NMR spectrum ( $\delta$ , ppm): 20.7 q and 22.6 q ( $CH_3$ ), 31.0 d (CH in i-Pr), 50.1 d ( $C^2H$ ), 52.7 q and 52.8 q ( $OCH_3$ ), 54.0 d ( $C^3H$ ), 67.9 s (C-Br), 166.4 s, 167.4 s, 169.4 s and 169.7 s ( $C=O$ ).

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