

Cyclopropane Formation by Electroreductive Coupling of Activated Olefins and *gem*-Polyhalo Compounds

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Received 22 July 1997; accepted 15 January 1998

Abstract: Cyclopropyl derivatives have been prepared with satisfactory yields by electroreductive coupling of activated olefins and *gem*-polyhalo compounds. The reaction is efficient when the olefin is more easily reduced than the organic halide. Two types of intermediates can be involved to lead to the products. The radical anion of the olefin can react with the halo compound by electron-transfer followed by radical coupling, or be reduced into the dianion which reacts by nucleophilic displacement.

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INTRODUCTION

The most common way to prepare cyclopropanes involves the addition of a carbene or equivalent to an olefinic bond. Carbene or carbenoid intermediates derived from diazoalkanes or *gem*-dihalo compounds are usually electrophilic and therefore add more rapidly to electron-rich than to electron-deficient olefins¹. C₃-ring forming condensations from activated olefins thus usually require the use of carbanions bearing a good leaving group at the α -position such as the sulfoxonium ylides² or the α -halo enolates. An alternative to the Simmons-Smith reaction, and which is compatible with the use of activated olefins, has however been developed by Kanař *et al.*³ They showed that nickel or cobalt complexes can be used in the presence of Zn as reductant to carry out the cyclopropanation of electron-deficient olefins with CH₂Br₂ and other *gem*-dihaloalkanes. Electrochemistry has also alternatively been used to perform the cyclopropanation of activated olefins. Thus Baizer and Chroma⁴ investigated the electroreductive coupling between CCl₄ or CCl₃CO₂Et with various Michael acceptors. Chemical yields of cyclic products were between 10 and 20%. More recently, Tallec *et al.*⁵ showed that the α -halomalonate anion can be formed either by deprotonation of monohalomalonate or by electroreduction of the corresponding dihalo compound and leads to the cyclopropane derivative by addition to Michael acceptors.

We have already reported results on the electroreductive cyclocondensation of dihalo compounds and activated olefins using the sacrificial anode based procedure.⁶ The method has been found convenient to perform C₅- and C₆-ring formation, and also, though based on only few results, C₃-ring formation. We have now investigated more thoroughly this reaction to delineate its application to cyclopropane formation.

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RESULTS

Our previously reported results indicated that coupling between CH_2Br_2 and dimethyl maleate, or of CH_2Cl_2 with methyl cinnamate led to *ca.* 40 % yield of the corresponding cyclopropyl product.^{6a} The coupling between PhCHCl_2 and methyl acrylate also gave 30 % of the corresponding cyclopropane. The reactions were conducted in an undivided cell fitted with an aluminum anode and a stainless-steel cathode. The solvent supporting-electrolyte was *N*-methylpyrrolidone (NMP) containing ammonium salts. These cyclopropanations were not optimized at that time. We have since tried to extend the method to various polyhalo compounds, either *gem*-dichloro or -dibromo compounds, or substituted trichloromethanes, and various activated olefins.

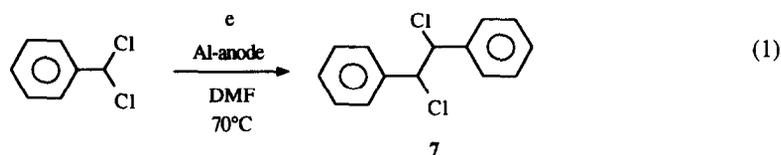
In direct electroreductive coupling reactions between two reagents, their reduction potential relative to each other is a key parameter. Two cases have to be considered depending on whether the olefin or the *gem*-dihalide is the most easily reduced of the two reagents. A Michael-type addition occurs when the halo compound is easier to reduce than the olefin. Alternatively, the reduced olefin will react with the halo compound. The reduction potentials of the reagents used were measured in DMF at a gold electrode. Values, referred to saturated calomel electrode (SCE), have been compiled in Table 1.

It can be seen that the reduction potentials of the various halo compounds range from -0.6 to -2.85 V/SCE. The reduction potentials of typical activated olefins are between -1.45 V (dimethyl maleate) and -2.15 V (methyl acrylate). In the first part of this study dimethyl maleate and dimethyl fumarate have been used in combination with all the halo compounds. Since the reduction potential of these olefins is about halfway between the extreme values of the reduction potentials of the halo compounds they can help to discriminate the two reaction mechanisms referred to above.

The reactions were conducted according to the method previously described.^{6a} DMF was found to be more convenient than NMP for these reactions. The electrolysis of mixtures of 10 mmoles of the olefin and 20 mmoles of the halo compound in 60 ml of DMF were run at constant current intensity ($I = 0.1$ A) up to full consumption of the unsaturated compound. The reaction temperature was found to be an important factor depending on the reagents involved. The results are given in Table 2.

In all cases dimethyl fumarate was found to be more efficient than dimethyl maleate. The dimethyl cyclopropanedicarboxylate obtained is always the *trans* compound whatever the (*E*) or (*Z*) starting olefin. This rules out definitely a possible carben route to the products. Yields reported in Table 2, and in the equations are of isolated products. The by-products were formed from both the olefinic reagent (dimerisation) and the halo compound (reduction or dimerisation).

gem-Dichloro compounds are not reactive in the coupling with maleate or fumarate diester except the case of α,α -dichlorotoluene. In the latter case (Table 2, entries 5, 6) the reaction gave 25 % of the cyclopropyl product **3** with dimethyl fumarate at room temperature. At a higher temperature the only product formed was the dimer **7** of benzal chloride (eq 1).



The cyclopropanation of dimethyl fumarate can be obtained in medium to good yields with *gem*-dibromoalkanes except methyl dibromoacetate. Products yields at 70 °C were higher than at room temperature. Notably, with 2,2-dibromopropane (Table 2, entry 1) a 60% yield of the cyclopropyl adduct 1 was obtained at 70 °C instead of 30% at 20 °C.

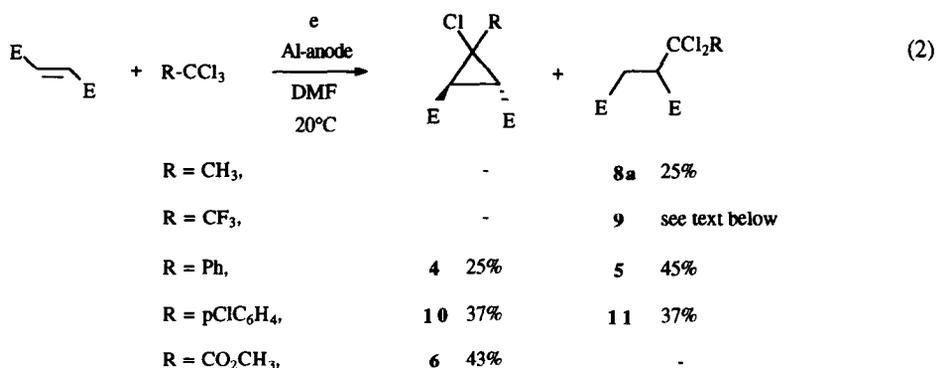
Table 1. Reduction Potentials of *gem*-Polyhalo Compounds and Activated Olefins⁽¹⁾

| halo compound | $E_{V/SCE}$ | olefin ⁽²⁾ | $E_{V/SCE}$ |
|--|-------------|-----------------------|-------------|
| dimethyl dibromomalonate | - 0.6 | | - 1.45 |
| CBr ₄ | - 0.6 | | |
| BrCCl ₃ | - 1 | | - 1.6 |
| NC-CCl ₃ | - 1.05 | | |
| CCl ₄ | - 1.4 | | |
| Cl ₃ CCO ₂ CH ₃ | - 1.6 | | - 1.8 |
| PhCCl ₃ | - 1.7 | | |
| CF ₃ CCl ₃ | - 1.7 | | |
| <i>p</i> -ClC ₆ H ₄ CCl ₃ | - 1.82 | | - 1.9 |
| (CH ₃) ₂ CBr ₂ | - 2.1 | | |
| CH ₂ Br ₂ | - 2.1 | | - 2.05 |
| PhCHCl ₂ | - 2.2 | | |
| CH ₃ CCl ₃ ⁽³⁾ | - 2.26 | | |
| CH ₃ CHBr ₂ | - 2.3 | | |
| CH ₂ Cl ₂ | - 2.6 | | - 2.15 |
| CH ₃ CHCl ₂ | - 2.85 | | |

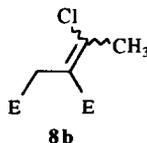
⁽¹⁾DMF, NBu₄BF₄ : 0.1 mol/l; working electrode : gold; auxiliary electrode : platinum; reference electrode : SCE.

⁽²⁾E = CO₂CH₃, ⁽³⁾see ref 7.

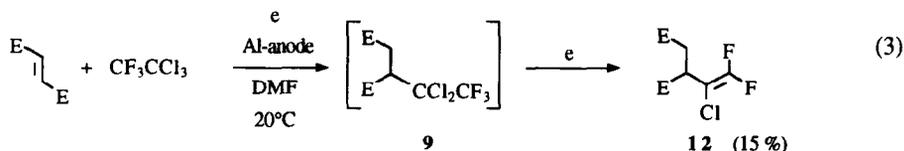
The coupling was found to be slightly more efficient with substituted trichloromethanes, but two products were indeed obtained as shown in eq 2, the expected cyclic adduct along with a monoalkylated product.



Actually, the monoalkylated product was obtained for R = CH₃ or CF₃ (respectively **8a**, **9**) along with traces of the cyclopropyl product. With R = CH₃, we observed the formation of the olefinic product **8b** due to loss of HCl.



In addition, with CF₃CCl₃ the non-cyclic adduct was converted *in situ* into the unsaturated product **12** as a result of the further reduction of **9** (eq 3).



These two reactions with CH₃CCl₃ and with CF₃CCl₃ could not be carried out at 70 °C because of the low boiling point of these halides.

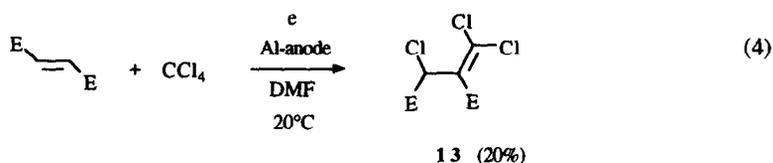
With α,α,α -trichlorotoluene the monoalkylated product **5** was obtained in good yields as the major product at room temperature but the cyclic adduct was mostly obtained at 70 °C (Table 2, entries 7, 8). A similar behavior was observed with *p*-ClC₆H₄CCl₃ (eq 2). On the contrary with methyl trichloroacetate the cyclic product **6** was obtained in good yields which did not depend on the temperature, and the alkylated product was formed as traces (Table 2, entries 9, 10 or eq 2).

We have also examined the reactivity of tetrahalomethanes, CCl₄, CBr₄ and BrCCl₃. With CCl₄ we obtained the uncyclised unsaturated product **13** in 20% yield (eq 4). With CBr₄ or BrCCl₃ no condensation product was obtained.

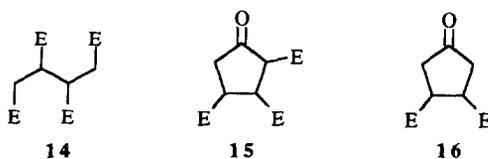
Table 2. Electrochemical Coupling of Dimethyl Fumarate or Maleate and *gem*-Polyhalo Compounds at Room Temperature and at 70°C.⁽¹⁾

| entry | halide (0.3 mol/l) | olefin ⁽²⁾ (0.15 mol/l) | product | n° | isolated yield % RT | 70°C |
|-------|--|---------------------------------------|---------|----|------------------------|------|
| 1 | (CH ₃) ₂ CBr ₂ | | | 1 | 30 | 60 |
| 2 | " | | | 1 | 25 | 34 |
| 3 | CH ₃ CHBr ₂ | | | 2 | 25 | 35 |
| 4 | " | | | 2 | 18 | 30 |
| 5 | PhCHCl ₂ | | | 3 | 25 | 0 |
| 6 | " | | | 3 | 10 | 0 |
| 7 | PhCCl ₃ | | | 4 | 25 | 34 |
| | | | | 5 | 45 | 7 |
| 8 | " | | | 4 | 0 | 16 |
| | | | | 5 | 0 | 1 |
| 9 | Cl ₃ CCO ₂ CH ₃ | | | 6 | 43 | 40 |
| 10 | " | | | 6 | 20 | 17 |

⁽¹⁾DMF (60ml), NBu₄Br (0.03 mol/l), NBu₄I (7.10⁻³ mol/l), I = 0.1 A, under argon, aluminum rod anode, stainless steel grid cathode. ⁽²⁾E = CO₂CH₃.

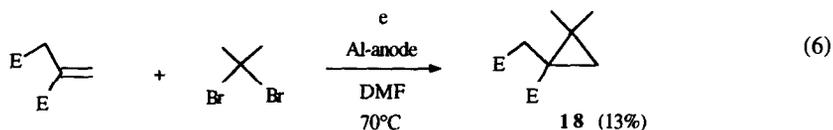
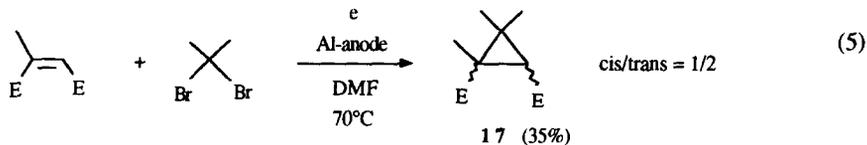


The main side-reactions observed involve maleic or fumaric diester. One product is the dihydrodimer **14** already obtained by electrochemical procedures. Another product **15** was formed through a Dieckmann reaction from the intermediate first formed in the dimerisation reaction. The triester **15** obtained is not thermally stable and is detected by GC-MS analysis as the diester **16**. We have been able to differentiate these two compounds by comparison to an authentic sample of **15** prepared by way of a literature method⁸ from **14**.



Reductive dimerisation of the halo compound was also observed in some cases. This notably occurred with benzal chloride which gave dichlorodibenzyl **7** as a 90/10 diastereomeric mixture in appreciable amount at room temperature and as the major product at 70 °C (eq 1). On the contrary less than 5% of dimer was found with the other trichloromethyl derivatives from which the main by-product was the reduction product.

The reaction was also studied with methyl citraconate (eq 5) and methyl itaconate (eq 6):

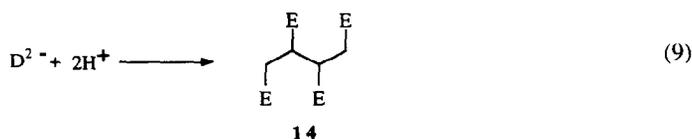


DISCUSSION

We have already mentioned that the relative reduction potential of the two reagents involved in the cyclocondensation is of importance for the reaction to proceed selectively. Some reagents are more easily reduced than dimethyl maleate or fumarate. This is the case for CBr_4 , BrCCl_3 , E_2CBr_2 ($\text{E} = \text{CO}_2\text{CH}_3$) and Cl_3CCN . With these reagents we can expect a Michael addition of the corresponding anion to the olefin followed by internal displacement to give the cyclopropane. This did not occur, and only the reduction product of the halide was obtained. With CCl_4 , and using a large excess of it, some amount of radical-addition product **13** was obtained (eq 4).

A second group of *gem*-polyhalo compounds includes those ($\text{Cl}_3\text{CCO}_2\text{CH}_3$, CF_3CCl_3 , PhCCl_3 , and $p\text{-ClPhCCl}_3$) who have a reduction potential close to the reduction potential of dimethyl fumarate or maleate. With these halo compounds the coupling products were obtained either as cyclic or non-cyclic compounds. Interestingly the reaction was found to be more efficient with fumaric than with maleic diester. This can be explained by the easier reduction of the former as compared to its stereoisomer as well as to the halo compounds. It can be inferred from these results that the alternative route involving the preferential reduction of the activated olefin over the reduction of the polyhalo compound is more efficient. In keeping with this is the observed efficiency in reactions involving *gem*-dibromo or dichloro compounds which are reduced at less than -2V/SCE .

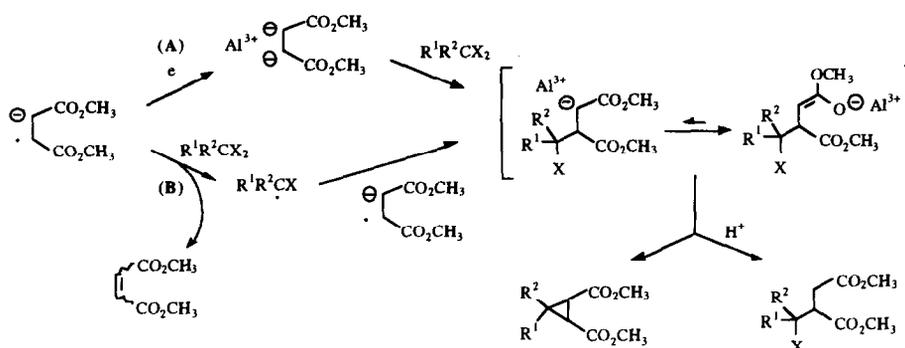
The electrochemical reduction of maleic or fumaric diesters in aprotic solvents and in the presence of ammonium salts has been already investigated.⁹ In the absence of electrophile the radical anion which is first formed (eq 7), dimerises according to eq 8 where A stands for maleic or fumaric diesters, and D for their dimer.



We have also already found that when the reduction of A is conducted in an undivided cell and in the presence of a sacrificial aluminum anode the radical anion may be further reduced into the dianion as we previously suggested in order to account for a more efficient cyclocondensation between 1,3-dibromopropane and dimethyl maleate when the reaction is conducted in the presence of an Al-anode as compared to the reaction conducted in a divided cell.^{6b}

Thus two types of intermediates can be involved to lead to the products. The first formed radical anion can either be reduced into the dianion to further react by nucleophilic displacement with $\text{R}^1\text{R}^2\text{CX}_2$ (Scheme 1, pathway A), or react with $\text{R}^1\text{R}^2\text{CX}_2$ by electron transfer⁹ followed by coupling of the thus formed radical with the radical anion of the olefin (Scheme 1, pathway B). It is likely that in the reaction conditions, the two reactions may occur.

The involvement of the radical anion may notably explain the formation of the dimer of the olefin **14** (according to eq 7-9), as well as the ensuing Dieckmann-reaction derived product **15**. Also, electron transfer from the radical anion to the *gem*-polyhalo compound leads to a α -halo radical which can dimerise, such a side reaction being more or less important as mentioned above.



Scheme 1

CONCLUSION

In conclusion, the electrochemical reduction of activated olefins in the presence of *gem*-polyhalo compounds might be used to prepare cyclopropanoid derivatives. The key intermediate may be a radical anion or a dianion, both being able to react with halo compounds by, respectively, electron-transfer and nucleophilic displacement. With halo compounds which are more easily reduced than the olefin, the expected Michael addition did not occur.

EXPERIMENTAL SECTION

¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker AC-200 (200 MHz) or AM-300 (300 MHz) spectrometer. Mass spectra (electron impact) were obtained on a Finnigan ITD 800 spectrometer coupled to a Varian 3300 chromatograph with a SIL-5 CP capillary column. High-resolution mass spectral analyses were performed by "Service de Microanalyse du CNRS, Lyon". Gas chromatography was performed on a Varian 3300 chromatograph equipped with a SIL-5 CP capillary column. All reagents and supporting electrolytes were used as obtained commercially.

General procedure: The reactions were conducted in an undivided cell fitted with an aluminum rod as the anode and a stainless steel grid as the cathode (area: *ca.* 40 cm²). A solution of the activated olefin (10 mmol) and the halo compound (20 mmol) in DMF (60 ml) containing NBu₄Br (2.2 mmol) and NBu₄I (0.5 mmol) was electrolysed at constant current density (*ca.* 2 A dm⁻²) until the olefin had been consumed. The reaction mixture was poured into a cold mixture of 1 M HCl (50 ml) and diethyl ether (50 ml). The layers were separated, and the aqueous layer was extracted with diethyl ether (25 ml). The combined ethereal extracts were washed with water, dried over Na₂SO₄, and evaporated. Products were isolated as follows by column chromatography on silica gel (230 - 400 mesh) using pentane-ether as eluent.

1: dimethyl *trans*-3,3-dimethylcyclopropane-1,2-dicarboxylate: (C₉H₁₄O₄); MW: 186; RN: 16601-23-3. Pentane/ether: 90/10; obtained: 1.12 g (60% yield); liquid. ¹H-NMR (200 MHz, CDCl₃) δ 3.7 (OCH₃, 6H, s), 2.2 (H-1 and H-2, 2H, s), 1.2 (H-4 and H-5, 6H, s); ¹³C-NMR (50 MHz, CDCl₃) δ ¹³C=O: 170.1; OCH₃: 51.2; C-1, C-2: 33; C-3: 29.7; C-4, C-5: 19.8; EI-MS *m/z* 155, 127 (base peak), 95, 67; IR ν cm⁻¹ (CCl₄) 1735.

2: dimethyl 3-methylcyclopropane-1 α ,2 β -dicarboxylate: (C₈H₁₂O₄); MW: 172; RN: 28363-79-3.

Pentane/ether: 95/5; obtained: 0.60 g (35% yield); liquid. ¹H-NMR (200 MHz, CDCl₃) δ 3.63 (OCH₃, 3H, s), 3.62 (OCH₃, 3H, s), 2.25 (H-1, 1H, dd, ³J = 9.5, 4.8 Hz), 2.04 (H-2, 1H, dd, ³J = 5.8, 4.8 Hz), 1.79 (H-3, 1H, m), 1.2 (H-4, 3H, d, ³J = 6 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ $\underline{\text{C}}\text{O}$: 172.3, 170.3; OCH₃: 51.9, 51.6; C-1, C-2: 28.2, 27.7; C-3: 23.7; C-4: 11; EI-MS m/z 141, 113 (base peak), 81, 59, 53; IR ν cm⁻¹ (CCl₄) 1735.

3: dimethyl 3-phenylcyclopropane-1 α ,2 β -dicarboxylate: (C₁₃H₁₄O₄); MW: 234; RN: 20098-66-2.

Pentane/ether: 80/20; obtained: 0.59 g (25% yield); solid: mp = 82.5-84.3°C (lit.^{10a,b} 82-83°C). ¹H-NMR (200 MHz, CDCl₃) δ 7.3 (Ph, 5H, m), 3.8 (OCH₃, 3H, s), 3.5 (OCH₃, 3H, s), 3.10 (H-3, 1H, dd, ³J = 10, 6.4 Hz), 2.85 (H-1, 1H, dd, ³J = 6.4, 4.8 Hz), 2.63 (H-2, 1H, dd, ³J = 10, 4.8 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ $\underline{\text{C}}\text{O}$: 172, 168.8; C-4: 134; C-5, C-6, C-7: 128.8, 128.1, 127; OCH₃: 52.3, 51.9, C-3: 32.7; C-1, C-2: 29.8, 25.8; EI-MS m/z 203, 175, 115 (base peak); IR ν cm⁻¹ (CCl₄) 1735.

4: dimethyl 3-chloro-3-phenylcyclopropane-1 α ,2 β -dicarboxylate (new compound): (C₁₃H₁₃ClO₄); MW: 268.5.

Pentane/ether: 80/20; obtained: 0.92 g (34% yield); solid: mp = 99-101°C; RN for diethyl ester: 116497-51-9, (1 α ,2 β -[39882-13-4]). ¹H-NMR (200 MHz, CDCl₃) δ 7.5-7.3 (Ph, 5H, massifs), 3.85 (OCH₃, 3H, s), 3.55 (OCH₃, 3H, s), 3.2-3.0 (H-1 and H-2, 2H, dd, ³J = 7 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ $\underline{\text{C}}\text{O}$: 167.4; 167.1; C-4: 137.3; C-5, C-6, C-7: 129.2, 128.85, 128.84; OCH₃: 52.9, 52.5, C-3: 51.2; C-1, C-2: 35.2, 33; EI-MS m/z 233, 210, 208, 201, 149 (base peak), 129, 115, 77, 59; IR ν cm⁻¹ (CCl₄) 1735. Anal. Calcd. for C₁₃H₁₃ClO₄: C, 58.11; H, 4.87; Cl, 13.20. Found: C, 58.03; H, 4.94; Cl, 13.22.

5: dimethyl 2-[(1,1-dichloro-1-phenyl)methyl]butane-1,4-dioate (new compound): (C₁₃H₁₄Cl₂O₄); MW: 305.

Pentane/ether: 80/20; obtained: 1.374 g (45% yield); solid: mp = 30°C. ¹H-NMR (200 MHz, CDCl₃) δ 7.7 (H-7, 2H, m), 7.4 (H-8, H-9, 3H, m), 3.83 (H-2, 1H, dd, ³J = 11 Hz, 3Hz), 3.6 (OCH₃, 3H, s), 3.45 (OCH₃, 3H, s), 3.3-2.7 (H-3, 2H, 2dd, ²J = 18 Hz, ³J = 11, 3 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ $\underline{\text{C}}\text{O}$: 171.2; 169; C-6: 140.6; C-7, C-8, C-9: 129.3, 128, 126.5, C-5: 91; C-2: 58; OCH₃: 52, 51.9; C-3: 34.3; EI-MS m/z 271/269, 239, 237 (base peak), 209, 161, 159, 149, 129, 115, 59; FAB-HR-MS calcd for C₁₃H₁₄Cl₂O₄ (M+Li)⁺ m/z 311.0429, found 311.0417; IR ν cm⁻¹ (CCl₄) 1745, 1550, 1450.

6: trimethyl 1-chlorocyclopropane-1,2 α ,3 β -tricarboxylate: (C₉H₁₁ClO₆); MW: 251.

Pentane/ether: 80/20; obtained: 1.08 g (43% yield); liquid; RN for triethyl ester:⁴ 34405-15-7. ¹H-NMR (200 MHz, CDCl₃) δ 3.7 (OCH₃, 6H, s), 3.65 (OCH₃, 3H, s), 3.15-2.8 (H-2 and H-3, 2H, dd, ³J = 7.4 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ $\underline{\text{C}}\text{O}$: 166.2, 165.3, 164.3; OCH₃: 53.4, 52.5, 52.4; C-1: 45.6; C-2, C-3: 34.7, 32.6; EI-MS m/z 221/219, 193, 191 (base peak), 163, 135, 113, 59; IR ν cm⁻¹ (CCl₄) 1740.

7: 1,2-dichloro-1,2-diphenylethane: (C₁₄H₁₂Cl₂); MW: 251, RN: 5963-49-5.

Pentane; obtained: 0.762 g (two diastereoisomeres *R***R** and *R***S**: 90-10; 61% yield); solid; mp = 93°C (lit.¹¹ 90-92°C *R***R**; 191-193°C *R***S**). ¹H-NMR (200 MHz, CDCl₃) δ 7.1 (Ph, 10H, s), 5.2 (H-1, 2H, s); ¹³C-NMR (50 MHz, CDCl₃) δ C-2: 137.4; C-3, C-4, C-5: 128.8, 128.7, 128.3; C-1: 67.8; EI-MS m/z 252/250, 179, 127/125 (base peak); IR ν cm⁻¹ (CCl₄) 1600, 1500, 1450.

8a: dimethyl 2-(1,1-dichloroethyl)butane-1,4-dioate (new compound): (C₈H₁₂Cl₂O₄); MW: 243.

Pentane/ether: 90/10; obtained: 0.607 g (25% yield, purity: 90%, 10% of **8b** formed by loss of HCl); liquid. ¹H-NMR (200 MHz, CDCl₃) δ 3.7 (OCH₃, 3H, s), 3.61 (OCH₃, 3H, s), 3.5 (H-2, 1H, dd, ³J = 10.4, 4 Hz), 3.2–2.85 (H-3, 2H, 2dd, ²J = 17.3 Hz, ³J = 10.4, 4 Hz), 2.2 (H-6, 3H, s); ¹³C-NMR (50 MHz, CDCl₃) δ CO: 171.1, 169.3; C-5: 87.6, C-2: 56.3, OCH₃: 52.2, 51.7; C-6: 35.6, C-3: 34; EI-MS m/z 246/244/242, 213/211, 175 (base peak), 147, 113, 105, 89, 59, 53; FAB-HR-MS calcd for C₈H₁₂Cl₂O₄ (M+Li)⁺ m/z 249.0273, found 249.0290; IR ν cm⁻¹ (CCl₄) 1735.

8b: dimethyl 2-(1-chloroethylidene)butane-1,4-dioate (new compound): (C₈H₁₁ClO₄); MW: 206.5.

Pentane/ether: 90/10; **8b** was obtained from **8a** by reaction of sodium methylate in methanol: 0.20 g (95% yield); liquid. ¹H-NMR (200 MHz, CDCl₃) δ 3.68 (OCH₃, 3H, s), 3.62 (OCH₃, 3H, s), 3.53 (H-3, 2H, s), 2.52 (H-6, 3H, s); ¹³C-NMR (50 MHz, CDCl₃) δ CO: 170.5, 165.8; C-2, C-5: 148.6, 123, OCH₃: 52, 51.9; C-3: 36.7, C-6: 25.5; EI-MS m/z 206/208, 175/177, 171 (base peak), 139, 111, 53; FAB-HR-MS calcd for C₈H₁₁ClO₄ (M+Li)⁺ m/z 213.0506, found 213.0516; IR ν cm⁻¹ (CCl₄) 1740.

9: dimethyl 2-(1,1-dichloro-2,2,2-trifluoroethyl)butane-1,4-dioate (new compound): (C₈H₉Cl₂F₃O₄); MW: 297.

Pentane/ether: 90/10; obtained: 0.080 g (isolated at the half time of the reaction, yield non determined); liquid. ¹H-NMR (200 MHz, CDCl₃) δ 3.7–3.6 (H-2, 1H, dd, ³J = 11, 3 Hz), 3.7 (OCH₃, 3H, s), 3.64 (OCH₃, 3H, s), 3.3–2.9 (H-3, 2H, 2dd, ²J = 17 Hz, ³J = 11, 3 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ CO: 170.4, 167.9; C-6: 121.6 (q, ¹J = 285 Hz); C-5: 84.2 (q, ²J = 35.7 Hz); OCH₃: 52.7, 52; C-2: 49.9; C-3: 33.7. ¹⁹F-NMR (188 MHz, CDCl₃) δ -76.2 (F-6, 3F, s); EI-MS m/z 267/265, 231/229, 217, 201, 143, 113, 59 (base peak); EI-HR-MS calcd for C₈H₉Cl₂F₃O₄ (M⁺ - OCH₃) m/z 264.9646, found 264.9640; IR ν cm⁻¹ (CCl₄) 1735.

10: dimethyl 3-chloro-3-(4-chlorophenyl)cyclopropane-1α,2β-dicarboxylate (new compound): (C₁₃H₁₂Cl₂O₄); MW: 303.

Pentane/ether: 80/20; obtained: 1.12 g (37% yield); solid; mp = 119,5–120 °C; RN for diethyl ester: 116377-05-0, 1,2-*t*-[116497-52-0]. ¹H-NMR (200 MHz, CDCl₃) δ 7.3 (H-5 and H-6, 4H, m), 3.8 (OCH₃, 3H, s), 3.5 (OCH₃, 3H, s), 3.1 (H-1 and H-2, 2H, s), ASIS effect (Aromatic Solvent Induced Shift) in benzene-D₆: 3.6–3.3 (H-1 and H-2, 2H, dd, ³J = 7.4 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ CO: 167.1, 166.7; C-4, C-7: 135.6, 135; C-5, C-6: 129.9, 128.9; OCH₃: 52.7, 52.4; C-3: 50.3; C-1, C-2: 35, 33; EI-MS m/z 273/271, 267, 244, 185, 183 (base peak), 149, 114, 59; IR ν cm⁻¹ (CCl₄) 1735, 1550, 1440. Anal. Calcd. for C₁₃H₁₂Cl₂O₄: C, 51.51; H, 3.99; Cl, 23.39. Found: C, 51.87; H, 4.03; Cl, 23.45.

11: dimethyl 2-[1,1-dichloro-1-(4-chlorophenyl)methyl]butane-1,4-dioate (new compound): (C₁₃H₁₃Cl₃O₄); MW: 339.5.

Pentane/ether: 80/20; obtained: 1.25 g (37% yield); solid; mp = 30 °C. ¹H-NMR (200 MHz, CDCl₃) δ 7.7–7.2 (H-7 and H-8, 4H, dd, ³J = 8.8 Hz), 3.75 (H-2, 1H, dd, ³J = 11, 3 Hz), 3.55 (OCH₃, 3H, s), 3.4 (OCH₃, 3H, s), 3.25–2.75 (H-3, 2H, 2dd, ²J = 18 Hz, ³J = 11, 3Hz); ¹³C-NMR (50 MHz, CDCl₃) δ CO: 171.1, 168.7; C-6, C-9: 139.3, 135.4; C-7, C-8: 128.2, 128.1; C-5: 90.3; C-2: 57.9; OCH₃: 52.2, 52; C-3: 34.3; EI-MS m/z 307/305/303, 273/ 271 (base peak), 243, 183, 149, 115, 59; FAB-HR-MS calcd for C₁₃H₁₃Cl₃O₄ (M+Li)⁺ m/z 345.0039, found 345.0058; IR ν cm⁻¹ (CCl₄) 1750, 1600, 1550, 1440.

12: dimethyl 2-(1-chloro-2,2-difluoroethenyl)butane-1,4-dioate (new compound): (C₈H₉ClF₂O₄); MW: 242.5.

Pentane/ether: 90/10; obtained: 0.37 g (15% yield, purity > 98%); liquid. ¹H-NMR (200 MHz, CDCl₃) δ 3.68 (OCH₃, 3H, s), 3.63 (OCH₃, 3H, s), 4.0 (H-2, 1H, tt, ³J = 7 Hz, ⁴J(H-2, F-6) = 1.8 Hz), 3.1-2.45 (H-3, 2H, 2dd, ²J = 17 Hz, ³J = 7 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ C-4: 170.5; C-1: 169.1 (t, ⁴J(C-1, F-6) = 3.6 Hz; C-6: 154.3 (t, ¹J(C-6, F-6) = 287 Hz; C-5: 90.5-89.0 (dd, ²J(C-5, F-6) = 42, 23 Hz); OCH₃: 52.3, 51.5; C-2: 40.5; C-3: 32.6 (t, ⁴J(C-3, F-6) = 2Hz); ¹⁹F-NMR (188 MHz, CDCl₃) δ -86.4, -91 (F-6, 2F, dd, ²J = 35 Hz); EI-MS m/z 244/242, 213/211, 207 (base peak), 183, 155, 141, 125, 59; EI-HR-MS calcd for C₈H₉ClF₂O₄ (M⁺ - Cl) m/z 207.0469, found 207.0463; (M⁺ - OCH₃) m/z 210.9973, found 210.9954; IR ν cm⁻¹ (CCl₄) 1740.

13: dimethyl 2-chloro-3-[dichloromethylidene]succinate (new compound): (C₇H₇Cl₃O₄); MW: 261.5.

Pentane/ether: 90/10; obtained: 0.53 g (20% yield); liquid. ¹H-NMR (200 MHz, CDCl₃) δ 5.52 (H-1, 1H, s), 3.77 (OCH₃, 3H, s), 3.76 (OCH₃, 3H, s); ¹³C-NMR (50 MHz, CDCl₃) δ C=O: 166.1, 162.4; C-3: 135.7; C-2: 128.6; C-1: 55.6; OCH₃: 53.8, 52.8; EI-MS m/z 229/227/225, 203/201, 109, 107, 79, 59 (base peak); IR ν cm⁻¹ (CCl₄) 1740, 1590. Anal. Calcd. for C₇H₇Cl₃O₄: C, 32.15; H, 2.70; Cl, 40.68. Found: C, 32.94; H, 2.87; Cl, 40.85.

14: tetramethyl butane-1,2,3,4-tetracarboxylate: (C₁₂H₁₈O₈); MW: 290, RN: 24261-13-0.

Pentane/ether: 80/20; obtained: 0.57 g (40% yield); solid; mp = 72-75°C (lit.^{12a,b} 75°C). ¹H-NMR (200 MHz, CDCl₃) δ 3.54 (OCH₃, 3H, s), 3.52 (OCH₃, 3H, s), 3.15 (H-2, 1H, m), 2.7-2.2 (H-3, 2H, 2dd, ²J = 17 Hz, ³J = 9.5 Hz, 4 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ C=O: 172.3, 171.5; OCH₃: 52, 51.7; C-2: 42; C-3: 32.8; EI-MS m/z 290, 259, 199, 198 (base peak), 167, 166, 139, 114, 59; IR ν cm⁻¹ (CCl₄) 1750; 1740.

15: trimethyl 4-oxocyclopentane-1,2,3-tricarboxylate: (C₁₁H₁₄O₇); MW: 258, RN: 67885-96-5.

Pentane/ether: 70/30; obtained: 0.392 g (30% yield); liquid. ¹H-NMR (200 MHz, CDCl₃) δ 3.9 (H-2, 1H, t, ³J = 11 Hz), 3.8 (OCH₃, 3H, s), 3.78 (OCH₃, 3H, s), 3.76 (OCH₃, 3H, s), 3.6 (H-3, 1H, d, ³J = 11 Hz), 3.2-3.4 (H-1, 1H, td, ³J = 11 Hz, 8.4 Hz); 2.9-2.5 (H-5, 2H, 2dd, ²J = 18.8 Hz, ³J = 11 Hz, 8.4 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ C-4: 204.4; C=O: 173.7, 172.8, 166.9; OCH₃: 52.3, 52.2, 52; C-1, C-2, C-3, C-5: 57.3, 46.6, 41.2, 41.1; EI-MS m/z 258, 227, 198 (base peak), 167, 139, 113, 59, 53; IR ν cm⁻¹ (CCl₄) 1775, 1750, 1745.

The triester **15** obtained is not thermally stable and was detected by GC-MS analysis as the diester **16**. We have been able to differentiate these two compounds by comparison to an authentic sample of **15** prepared by way of a literature method⁸ from **14**. **16** (dimethyl 4-oxocyclopentane-1,2-dicarboxylate): EI-MS m/z 200 (M, 12), 140 (74), 114 (72), 99 (17), 85 (23), 71 (70), 55 (100).

17: *cis*- and *trans*-dimethyl 1,3,3-trimethylcyclopropane-1,2-dicarboxylate (new compounds): (C₁₀H₁₆O₄); MW: 200.

Pentane/ether: 90/10; obtained: 0.69 g (35% yield, *cis* and *trans*); liquid.

cis-isomer: yield: 11%; ¹H-NMR (200 MHz, CDCl₃) δ 3.7 (OCH₃, 6H, s), 1.5 (H-2, 1H, s), 1.45 (H-4, 3H, s), 1.35-1.25 (H-5 and H-6, 6H, 2s); ¹³C-NMR (50 MHz, CDCl₃) δ C=O: 171.6, 170.4; OCH₃: 51.7, 51.4; C-2: 37.1; C-1: 35.6; C-3: 29; C-4: 22.6; C-5: 18.1; C-6: 17.9; EI-MS m/z 169, 141 (base peak), 109, 81, 79, 73, 67, 59, 53. EI-HR-MS calcd for C₉H₁₅O₃ (M⁺ - CHO) m/z 171.1021, found 171.1012; IR ν cm⁻¹ (CCl₄) 1735.

trans-isomer: yield: 24%; ¹H-NMR (200 MHz, CDCl₃) δ 3.6 (OCH₃, 3H, s), 3.55 (OCH₃, 3H, s), 2.2 (H-2, 1H, s), 1.4 (H-4, 3H, s), 1.2-1.05 (H-5 and H-6, 6H, 2s). ¹³C-NMR (50 MHz, CDCl₃) δ C=O: 172.6, 170.1; OCH₃:

51.7, 51; C-1: 36.4; C-2: 32.5; C-3: 30; C-4: 22.3; C-5: 15.3; C-6: 10.4; EI-MS m/z 169, 141 (base peak), 140, 125, 110, 109, 108, 81, 79, 73, 67, 59, 53; EI-HR-MS calcd for $C_9H_{13}O_3$ ($M^+ - OCH_3$) m/z 169.0864, found 169.0864; IR ν cm^{-1} (CCl_4) 1735.

18: methyl 2,2-dimethyl-1-methoxycarbonylmethylcyclopropane-1-carboxylate (new compound): ($C_{10}H_{16}O_4$); MW: 200.

Pentane/ether: 90/10; obtained: 0.255 g (13% yield); liquid. 1H -NMR (200 MHz, $CDCl_3$) δ 3.46 (OCH_3 , 3H, s), 3.45 (OCH_3 , 3H, s), 2.9 (H-6, 1H, d, $^2J = 17.5$ Hz), 1.3 (H-2, 1H, d, $^2J = 5$ Hz), 1-0.96 (H-4 and H-5, 6H, 2s); ^{13}C -NMR (50 MHz, $CDCl_3$) δ \underline{CO} : 172.7, 171.9; $\underline{OCH_3}$: 51.1, 51; C-6: 35.7; C-3: 30; C-2: 25.5; C-1: 24.5; C-4, C-5: 22, 20; EI-MS m/z 200, 169, 168, 140, 125, 109, 81 (base peak), 79, 53; EI-HR-MS calcd for $C_9H_{12}O_3$ ($M^+ - CH_3OH$) m/z 168.0786, found 168.0785; IR ν cm^{-1} (CCl_4) 1735.

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