was added $NaBH_4$ (1.90 g, 50 mmol), and the resulting mixture was refluxed for 1 h. Then the reaction mixture was poured into 0.1 N HCl (150 mL) and extracted with methylene chloride (2 × 75 mL). The organic layer was washed with $NaHCO_3$ (50 mL, saturated solution) and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave a syrup which was purified by a column chromatography (silica gel, 70–230 mesh, CH_2Cl_2/hexane, 1:2, and then 1:1 as eluant) to give first the title compound **25**. Yield: 2.14 g (50%). Mp: 112–114 °C (CCl_4/hexane). IR (KBr) ν 3376 (OH), 1726 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ (ppm): 6.76–7.59 (m, 9 H, arom), 5.46 (d, 1 H, J = 4.8 Hz, PhOCH), 5.36 (d, 1 H, J = 4.8 Hz, NCHAr), 4.70 (dd, 1 H, J = 12.6 Hz, J' = 7.2 Hz, CH_2OH), 4.61 (dd, 1 H, J = 12.6 Hz, J' = 4.8 Hz, CH_2OH), 2.21 (s, 1 H, CHSiMe$_3$), 1.43 (dd, 1 H, J = 4.8 Hz, J' = 7.2 Hz, OH), 0.26 (s, 9 H, SiCH_3), 0.16 (s, 9 H, SiCH_3). Anal. Calcd for $C_{23}H_{33}O_3NSi_2$: C, 64.58; H, 7.79; N, 3.27. Found: C, 64.87; H, 7.83; N, 3.30, and then 0.25 g (7%) of monodesilylated derivative of **25**. ^1H NMR ($CDCl_3$) δ (ppm): 6.71–7.41 (m, 9 H, arom), 5.46 (d, 1 H, J = 4.8 Hz, PhOCH), 5.28 (d, 1 H, J = 4.8 Hz, NCHAr), 4.57 (s, 2 H, CH_2OH), 2.95 (d, 1 H, J = 15.3 Hz, NCH_2SiMe$_3$), 2.40 (d, 1 H, J = 15.3 Hz, NCH_2SiMe$_3$), 2.25 (s, 1 H, OH), 0.11 (s, 9 H, $SiCH_3$).

Preparation of 4-(2′-Formylphenyl)-3-phenoxy-1-[bis(trimethylsilyl)methyl]azetidin-2-one (26). This compound was prepared using 3-carboxypyridinium dichromate/pyridine system following our procedure.[28] Yield: 1.12 g (88%). Mp: 126–128 °C (MeCN/H_2O). IR (KBr) ν 1754 (C=O), 1688 cm^{-1} (CHO). ^1H NMR ($CDCl_3$) δ (ppm): 9.99 (s, 1 H, CHO), 6.69–7.72 (m, 9 H, arom), 6.19 (d, 1 H, J = 4.8 Hz, NCHAr), 5.45 (d, 1 H, J = 4.8 Hz, PhOCH), 2.15 (s, 1 H, CHSiMe$_3$), 0.29 (s, 9 H, $SiCH_3$), 0.15 (s, 9 H, $SiCH_3$). Anal. Calcd for $C_{23}H_{31}O_3NSi_2$: C, 64.88; H, 7.35; N, 3.29. Found: C, 64.50; H, 7.28; N, 3.43.

Preparation of Benzocarbacephem 27. To a stirred solution of the aldehyde **26** (1.06 g, 2.5 mmol) in anhydrous tetrahydrofuran (13 mL) containing molecular sieves (1 g, 4A) was added, under nitrogen, tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF, 10 % mol). Immediately, a dark coloration appeared with slight exothermicity. After 90 min of stirring at room temperature, trimethylchlorosilane (0.33 mL, 2.6 mmol) was added and, after workup, the reaction crude was chromatographied (silica gel; eluant: CH_2Cl_2/hexane, 1/3), affording **27** [Yield: 0.26 g (40%) (syrup). ^1H NMR (δ ppm, $CDCl_3$): 7.02–7.35 (m, 9 H, arom), 6.64 (d, 1 H, J = 7.2 Hz, ArCH=), 6.16 (d, 1 H, J = 7.2 Hz, NCH=), 5.91 (d, 1 H, J = 4.2 Hz, NCHAr), 5.14 (d, 1 H, J = 4.2 Hz, PhOCH). MS (m/z) = 353 (M^+)] and **28** [Yield: 0.04 g (5%). ^1H NMR (δ ppm, $CDCl_3$): 9.96 (s, 1 H, CHO), 6.71–8.00 (m, 9 H, arom), 6.08 (d, 1 H, J = 4.8 Hz, NCHAr), 5.58 (d, 1 H, J = 4.8 Hz, PhOCH), 3.09 (d, 1 H, J = 15.3 Hz, NCH_2SiMe$_3$), 2.45 (d, 1 H, J = 15.3 Hz, NCH_2SiMe$_3$), 0.12 (s, 9 H, $SiMe_3$)].

Acknowledgment. This work has been supported by Departamento de Investigación del Gobierno Vasco (Eusko Jaurlaritzako Ikerkuntza-Saila), Project X:86:034. A grant from Ministerio de Educación y Ciencia (to J.M.G.) is gratefully acknowledged. We thank Dr. J. Garin from Departamento de Química Orgânica, Universidad de Zaragoza, for recording the mass spectra.

Electrochemical Coupling of Activated Olefins and Alkyl Dihalides: Formation of Cyclic Compounds

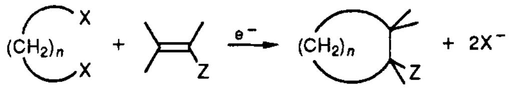
Yu-Wei Lu, Jean-Yves Nédélec,* Jean-Claude Folest, and Jacques Périchon

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique, CNRS U.M. 28, 2, rue Henri-Dunant, 94320 Thiais, France

Received June 20, 1989

The electrochemical coupling of dimethyl maleate, methyl cinnamate, 4-phenyl-3-buten-2-one, or methyl acrylate with dibromomethane, 1,3-dibromopropane, 1,4-dibromobutane, or other substituted alkyl dihalides gave satisfactory yields of cyclic products. The reactions were performed in an undivided cell fitted with a sacrificial aluminum anode, in N-methylpyrrolidone (NMP), at constant current, and at room temperature. The role of the anodically generated metallic ions in this cyclocondensation has been evidenced.

Cyclic and polycyclic compounds have great importance in synthetic chemistry, and new methods are constantly sought out with the aim of obtaining more simple and more efficient routes to cycle formation. Whereas ring closure of α–ω difunctional compounds is a straightforward method, more challenging is ring forming through bimolecular coupling, especially for cyclopentanation. Some efficient electrochemical intramolecular ring-forming reactions have already been described.[1] We thought in the wake of recent progress associated with the use of consumable anodes[2] that electroreductive organic chemistry could also offer a useful approach to bimolecular cyclocondensation. We describe here the synthesis of three-, five-, and six-membered alicyclic products by electroreductive coupling of electron-deficient olefins and alkyl dihalides (eq 1).



(1)

X = Br, Cl; n = 1–4; Z = electron –withdrawing group

Results

Results of the coupling reaction of various olefins and alkyl dihalides are given in Table I. Two typical experimental conditions were adopted according to the relative reduction potential of both the olefin and the opposed dihalide.[3] Thus, for the reaction involving dimethyl maleate and 1,3-dibromopropane, as an example of readily reduced olefin as compared to the dihalide, 2 equiv of 1,3-dibromopropane for 1 equiv of dimethyl maleate was mixed, in the range 0.3–0.8 M olefin, in N-methyl-

---

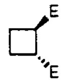
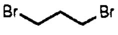
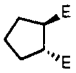
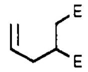
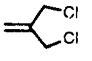
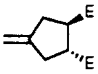
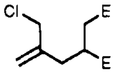
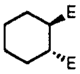
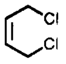
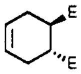
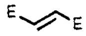
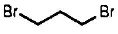
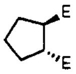
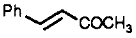
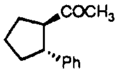
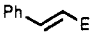
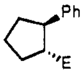
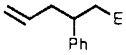
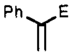
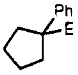
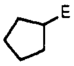
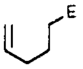
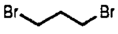
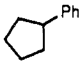
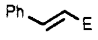
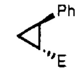
(1) (a) Rifi, M. R. *Tetrahedron Lett.* **1969**, *13*, 1046. (b) Giomini, C.; Inesi, A.; Zeuli, E. *J. Chem. Res., Synop.* **1983**, 280; *J. Chem. Res., Miniprint* **1983**, 2401. (c) Satoh, S.; Itoh, M.; Tokuda, M. *J. Chem. Soc., Chem. Commun.* **1978**, 481. (d) Little, R. D.; Fox, D. P.; Van Hijfte, L.; Dannecker, R.; Sowell, G.; Wolin, R. L.; Moëns, L.; Baizer, M. *J. Org. Chem.* **1988**, *53*, 2287.

(2) Recent papers and references therein: (a) Silvestri, G.; Gambino, S.; Filardo, G. *Tetrahedron Lett.* **1986**, *27*, 3429. (b) Silvestri, G.; Gambino, S.; Filardo, G. *Stud. Org. Chem.* **1987**, *30*, 287. (c) Heintz, M.; Sock, O.; Saboureau, C.; Troupel M. *Tetrahedron* **1988**, *44*, 1631. (d) Nédélec, J. Y.; Aït-Haddou-Mouloud, H.; Folest, J. C.; Périchon, J. *J. Org. Chem.* **1988**, *53*, 4720. (e) Sibille, S.; Mchareck, S.; Périchon, J. *Tetrahedron* **1989**, *45*, 1423. For a review on the sacrificial anode process: Chaussard, J.; Folest, J. C.; Nédélec, J. Y.; Périchon, J.; Sibille, S.; Troupel, M. *Synthesis*, in press.

(3) The following half-peak reduction potentials have been measured in NMP/NBu_4BF_4 at a gold cathode (value in volts vs SCE): dimethyl maleate, −1.6; methyl cinnamate, −1.85; methyl acrylate, −2.1; 4-phenyl-3-buten-2-one, −1.7; dibromomethane, −0.8; 1,2-dibromoethane, −1.4; 1,3-dibromopropane, −2.

0022-3263/90/1955-2503$02.50/0

Table I. Cycle Formation by Electroreductive Coupling of Activated Olefins and Alkyl Dihalides (E = CO_2Me)[a]

entry	olefin (mmol)	dihalide (mmol)	product (yield,[b] %)
1	 (10)	CH_2Br_2 (40)	 **C8** (41)
2	 (10)	 (40)	 **C11** (5)
3	 (10)	 (20)	 **C1** (50)  **L1** (10)
4	 (10)	 (20)	 **C2** (16)  **L2** (10)
5	 (10)	 (20)	 **C12** (40)
6	 (10)	 (20)	 **C13** (15)
7	 (10)	 (20)	 **C1** (18)
8	 (10)	 (20)	 **C3** (35)
9	 (10)	 (20)	 **C4** (66)  **L4** (5)
10	 (10)	 (20)	 **C5** (10)
11	 (40)	 (10)	 **C6** (10)  **L6** (9)
12	 (40)	 (10)	 **C7** (10)
13	 (10)	CH_2Cl_2 (40)	 *trans*-**C9** (40)
14	 (40)	$PhCHCl_2$ (10)	 *trans*-**C9** (30)

[a] NMP (37 mL), NBu_4BF_4 (0.3 mmol), NBu_4I (0.5 mmol), I = 0.2 A, anode aluminum rod, cathode stainless steel grid, 3 mol of electron/mol of olefin, room temperature, under argon. [b] Isolated yield relative to minor reactant.

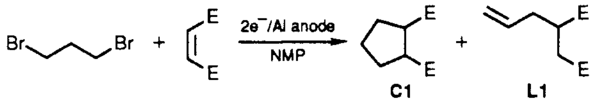
pyrrolidone (NMP) containing an ammonium salt as the supporting electrolyte. The electrolysis was carried out in a cylindrical undivided cell fitted with a rod of aluminum as the anode surrounded by a cylindrical stainless steel grid as the cathode. Three equivalents of electrons, relative to the olefinic compound, was passed at constant current with a current density ranging from 0.2 to 1 A/dm^2, at room temperature, and under argon. When both reagents are reduced at nearly the same potential, 4 times excess of the olefin relative to the halide was used, in order to favor the reduction of the unsaturated compound as, for instance, in reactions involving methyl acrylate (Table I, entries 11 and 13).

Three-, five-, and six-membered rings were easily formed in good yields. The stereochemistry of the 1,2-disubstituted cyclic adducts is mainly trans as anticipated for nonconcerted ring formation, with a trans/cis ratio larger than 10. Formation of four-membered cyclic compounds was not as satisfactory, since electroreduction of 1,2-alkyl dibromides readily gives ethylenic compounds, whereas the corresponding dichlorides are not reactive enough.

Reactions with diallyl dihalide (Table I, entries 4 and 6) did not afford high yields of the desired cyclic product: this is possibly due to their higher sensitivity to the reaction conditions, as compared to aliphatic dihalides, and their involvement in side reactions. No attempt was made to improve these reactions.

The formation of a noncyclic isomer as side product was generally observed in reactions leading to five-membered rings (Table I, entries 3, 9 and 11), whereas a chlorinated acyclic adduct (**L2**) was formed from methallyl dichloride along with the cyclic product (**C2**) (Table I, entry 4). Telomers from the activated olefins were also generally formed, but in yields not greater than 10%.

The influence of experimental parameters on ring formation was examined essentially in the coupling reaction between 1,3-dibromopropane and dimethyl maleate (eq 2).



(2)

E = $COOCH_3$

This reaction gives 50% and 10% yields, respectively, of the cyclic adduct **C1** and the acyclic one **L1** under the general experimental conditions given in Table I.

Factors that did not significantly affect the yield of **C1** are as follows: (i) the concentration of the reagents in the upper limit of 0.8 M for the olefin concentration and twice the amount of the alkyl dihalide; (ii) the current density up to 1 A/dm^2; (iii) the temperature in the range 0–60 °C.

The nature of the solvent (Table II) did not influence the overall yield of the two main products (the cyclic compound **C1** and its noncyclic isomer **L1**). However, it determined greatly the selectivity of the coupling reaction, i.e., the **C1**/**L1** ratio. Hexamethylphosphorous triamide (HMPT) is by far the best solvent regarding the ring formation, but it was rejected because of its toxicity. NMP or a 1/1 tetrahydrofuran–tetramethylurea (THF–TMU) mixture favored cyclic product formation, whereas other common solvents or mixtures of solvents gave rise to around 1/1 product mixtures. NMP was generally choosen for its higher conductivity over the THF–TMU mixture.

The supporting electrolyte had some influence on the selectivity, which we cannot satisfactorily explain, and very little influence on the overall yield. A convenient electrolyte was either NBu_4Br or NBu_4BF_4–NBu_4I mixture.

As for the anode,[4] we only got satisfactory results regarding the yield and the selectivity in the model reaction

---

[4] Some basic aspects of the sacrificial process have already been discussed in previous papers (see ref 2). The very nature of the reacting species has not been clearly elucidated so far. A true organometallic can be postulated as a transient intermediate, but it will not be possible to isolate it in solvents such as NMP or DMF.

Table II. Electrochemical Coupling of Dimethyl Maleate and 1,3-Dibromopropane: Influence of Solvent and Supporting Electrolyte[a]

entry	solvent	supporting electrolyte	faradays/mol[b]	product (yield %)[c] C1	L1	C1/L1	recovery of olefin (%)
1	HMPT	NBu_4I/NBu_4BF_4 (1.7/1)	1.3	76	22	3.4	5
2	NMP	NBu_4I/NBu_4BF_4 (1.7/1)	2.2	38	9.5	4	23
3	NMP	NBu_4Br	2	40	17.4	2.3	11
4	NMP	NBu_4I	2	27	33.7	0.8	0
5	NMP	LiCl	2	22	27.5	0.8	0
6	NMP	NBu_4Br/LiCl (1/1)	2.1	33	3	11	12
7	NMP	NBu_4BF_4/LiCl (1/1)	2	18	3.6	5	20
8	DMF	NBu_4I/NBu_4BF_4 (1.7/1)	2	20	13.3	1.5	27
9	THF/TMU (1:1)	NBu_4I/NBu_4BF_4 (1.7/1)	1.7	36	6	6	37
10	NMP/THF (1:1)	NBu_4I/NBu_4BF_4 (1.7/1)	0.6	26	26	1	40

[a] Dimethyl maleate (10 mmol), 1,3-dibromopropane (20 mmol), solvent (40 mL), supporting electrolyte (0.8 mmol), aluminum anode, stainless steel cathode, room temperature, under argon, I = 0, 2 A. [b] Usually ca 2 faradays/mol. Lower values indicate that electrode passivation importantly decreased the current intensity. [c] GC yield, relative to consumed olefin.

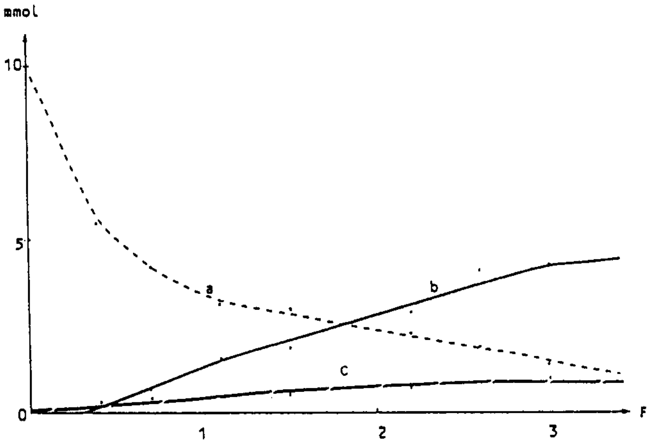


Figure 1. Product formation and olefin consumption vs electricity passed (faradays/mol of olefin) in the coupling reaction of dimethyl maleate and 1,3-dibromopropane: a, dimethyl maleate; b, **C1**; c, **L1**.

(eq 2) when aluminum was used as the anode material. With magnesium, the yield was low because of the degradation of the product as it was formed.[5] Other anodes were not convenient (yield <10%) because of the easy reducibility of the derived metallic ions as compared to the reagents.

These remarks apply to the other reactions, since they all were performed better in NMP containing an ammonium salt, with an aluminum rod as the anode and the cathode being either a stainless steel grid, glassy carbon, or nickel foam gauze.

Under these reaction conditions, the monitoring of amounts of reagents and products for the model reaction vs the charge passed (Figure 1) indicates rapid consumption of the unsaturated compound in the early stage of the electrolysis, corresponding to a charge of ca. one electron per molecule, followed by a slowing after 0.6 faraday.mol^{-1} has passed; total consumption of dimethyl maleate requires more than the theoretical amount of electricity. **L1** appears earlier than **C1**, and the rate of formation of the two products is roughly constant.

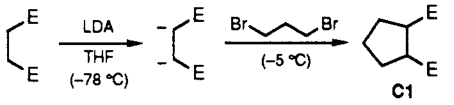
We have comparatively studied the reaction in a divided cell to show better evidence of the features of this process: in the presence of an ammonium salt as the only electrolyte (i.e., in NMP containing 1 M NBu_4Br), electroreduction of the reagent mixture of the model reaction gave only 3% yield of **C1**, whereas **L1** was formed in 35% yield. In the presence of 0.5–2 equiv of $AlBr_3$ vs the olefin in the cathodic compartment, the reaction was nearly suppressed; instead, telomerization of dimethyl maleate occurred. This clearly points out the role of the metallic ions derived from the anode and the requirement of their being produced as the reaction proceeds.

Discussion

The electroreductive alkylation of activated olefins has already been studied.[6] However, very few ring-forming electrochemical cross-couplings have been described so far: Baizer et al. detected moderate yields of substituted cyclopropanes from the reduction of *gem*-dihalides in the presence of activated olefins;[7] Degrand et al. described the electrochemical coupling of α,ω-dibromoalkanes with Schiff bases leading to pyrrolidines and piperidines[8a,b] and with carbonyl compounds leading to cyclic ethers.[8c] These reported syntheses were performed in divided cells, under controlled potentials.

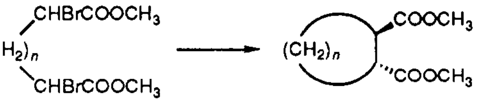
We found in this study that the ring-forming bisalkylation of activated olefins could not be performed satisfactorily in a classical divided cell in the presence of an ammonium salt. But, this reaction became feasible in an undivided cell, with aluminum as the consumable anode in NMP. Other media favored either the formation of a monoalkylated byproduct or the telomerization of the activated olefin.

This very simple method has been found convenient for the synthesis of three-, five-, and six-membered rings from very common reagents. It avoids the preparation of organometallic intermediates as, for example, in the closely related coupling of succinic dianion and 1,3-dibromopropane, leading to **C1** in the same yield[9] (eq 3), or the synthesis of an α,ω-dibromo derivative to be cyclized by electroreduction[1c] or by reacting it with NaCN[10] (eq 4).



(3)

E = COOCH$_3$



(4)

---

(5) Reductive degradation of organic compounds at the anodized magnesium has already been observed. See: Saboureau, C.; Troupel, M.; Përichon, J. *J. Appl. Electrochem.* **1990**, *20*, 97.

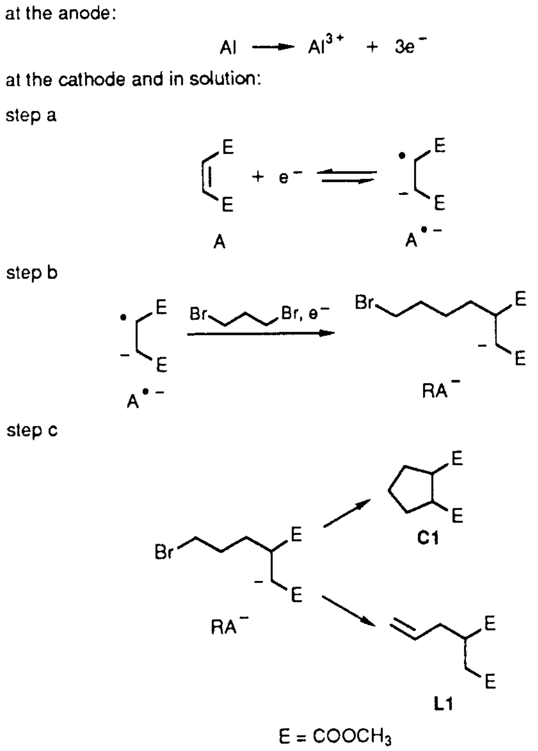
(6) Schäfer, H. *J. Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 911, and references therein.

(7) Baizer, M. M.; Chruma, J. L. *J. Org. Chem.* **1972**, *37*, 1951.

(8) (a) Degrand, C.; Grosdemouge, C.; Compagnon, P. L. *Tetrahedron Lett.* **1978**, *33*, 3023. (b) Degrand, C.; Compagnon, P. L.; Belot, G.; Jacquin, D. *J. Org. Chem.* **1980**, *45*, 1189. (c) Degrand, C.; Compagnon, P. C.; Gasquez, F.; Belot, G. *Electrochim. Acta* **1985**, *29*, 625.

(9) Wilkening, D.; Mundy, B. *Synth. Commun.* **1984**, *14*, 227.

Scheme I



We have shown that the nature of the sacrificial anode and the role of the anodically derived metallic ions are of great importance and, therefore, deserve some comment. Among the commonly used anodic metals in the sacrificial anode process (notably Mg, Zn, and Al), aluminum was found necessary for cyclization to occur. Indeed, as noted for the coupling of 1,3-dibromopropane and dimethyl maleate, in the absence of aluminum ions (i.e., in a divided cell), or at the early stage of the reaction in an undivided cell when the aluminum ion concentration is low, the formation of the monoalkylated product **L1** prevails. Thus, aluminum ions favor ring formation, but only if they are produced progressively as the reaction proceeds.

The electrochemical reduction of dimethyl maleate or fumarate (A) in DMF-NBu_4BF_4 has been thoroughly described[11] as giving the radical anion $A^{\bullet -}$, which dimerizes into the dianion D^{2-} (eqs 5 and 6). In the presence of an

$$A + e^- \rightarrow A^{\bullet -} \qquad (5)$$

$$2A^{\bullet -} \rightarrow D^{2-} \qquad (6)$$

alkyl halide (RX), an electron transfer from $A^{\bullet -}$ to the halide followed by reaction of the radical $R^\bullet$ either with the olefin or with the radical anion $A^{\bullet -}$ (eqs 7–10) has been postulated to account for formation of the adduct.[9b,c]

$$A^{\bullet -} + RX \rightarrow A + R^\bullet + X^- \qquad (7)$$

$$R^\bullet + A \rightarrow RA^\bullet \qquad (8)$$

$$RA^\bullet + e^- \rightarrow RA^- \qquad (9)$$

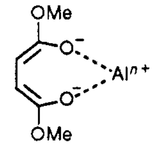
and/or

$$R^\bullet + A^{\bullet -} \rightarrow RA^- \qquad (10)$$

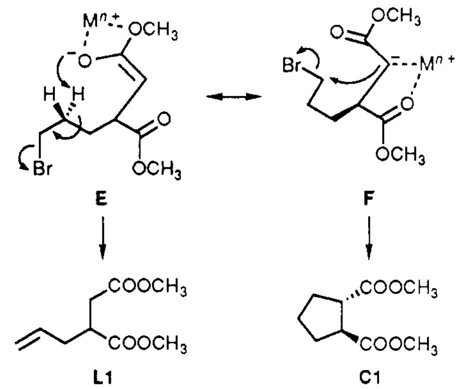
However, an S_N2 process (eq 11) should not be ruled out, at least in some cases.

$$A^{\bullet -} + RX \rightarrow RA^\bullet + X^- \qquad (11)$$

Chart I

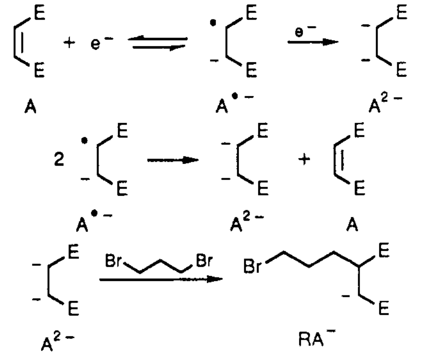


Scheme II



Applied to the cyclocondensation between 1,3-dibromopropane and dimethyl maleate, this would give the mechanism described in Scheme I, where step b summarizes a set of reactions, either eqs 7–9, eqs 7 and 10, or eqs 11 and 9.

An alternative mechanism could also be postulated, because of the presence of the aluminum ions necessary for ring formation. These ions can indeed complex with dimethyl maleate to favor its two-electron reduction, either at the cathode (eq 12) or through disproportionation of two radical anions (eq 13) to give an efficiently delocalized dianion, as depicted in Chart I, which will react with the dihalide (eq 14). This can account for the change of rate of consumption of dimethyl maleate at ca. 0.6 faraday. mol^{-1}, i.e., when the amount of aluminum ions is large enough to interact significantly with the unsaturated compound, and for the beginning of formation of **C1** (cf. Figure 1).



(12)

(13)

(14)

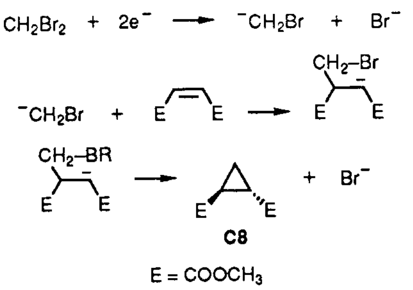
Through either route, intermediate RA^- should be formed to account for the formation of both cyclic and acyclic products (**C1** and **L1**). In the absence of aluminum, RA^- evolves into the acyclic product by HBr elimination, whereas with Al^{3+} the cyclic product is formed. This duality can be rationalized in terms of enolate ion resonance, with a major contribution of the enolate **E** in the presence of ammonium ions, whereas the multicharged aluminum ion would favor the carbon-centered form **F** as depicted in Scheme II. Since we observe the concurrent formation of both acyclic unsaturated adduct and five-membered ring, intramolecular HBr elimination, which requires a

---

(10) Fuson, R. C.; Kao, T. Y. *J. Am. Chem. Soc.* **1929**, *51*, 1537.

(11) (a) Yeh, L. S. R.; Bard, A. J. *J. Electrochem. Soc.* **1977**, *124*, 189. (b) Degrand, C.; Lund, H. *Nouv. J. Chim.* **1977**, *1*, 35. (c) Satoh, S.; Taguchi, T.; Itoh, M.; Tokuda, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 951.

Scheme III



convenient distance between the atoms involved, must occur.

Some reactions could proceed through a different mechanism. Indeed, when the dihalide is more easily reducible than the olefin, Michael addition is quite likely, followed by intramolecular substitution as exemplified in Scheme III for the coupling reaction between CH_2Br_2 and dimethyl maleate (Table I, entry 1). Another reaction of this class is the coupling of benzal chloride with methyl acrylate (Table I, entry 13). Though aluminum is also required in these Michael-type reactions, its role has not been investigated.

In conclusion, this work has resulted in a new method of electrochemical carbocyclization, which might be of special interest for synthesis of cyclopentanoid derivatives that are usually less easily formed than three- or six-membered rings. It has also given new insight in the electroreduction of activated olefins and organic halides when performed in the presence of aluminum ions. Finally, the synthetic interest of the novel electrochemical process based on anode dissolution is once again illustrated in this simple, room-temperature, one-pot cyclocondensation.

Experimental Section

^{1}H NMR spectra were recorded on a Varian 360A (60-MHz) or a Brucker AC 200 E (200-MHz) spectrometer. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer. Mass spectra were obtained on a Finnigan ITD 800 spectrometer coupled to a Varian 300 chromatograph with a DB-1 capillary column, either by electron impact or with CH_4 or NH_3 as the ionizing agent. Gas chromatography was performed on either a Delsi 330 chromatograph equipped with a OV 101 or OV 225 stainless steel ($^1/_8$ in. × 13 ft) column or a Varian 3700 equipped with a 25-m DB-1 capillary column. The electrochemical cell has been described previously.[2] Products were isolated by flash silica gel (230–240-mesh) column chromatography. High-resolution mass spectral analyses were performed by the service de Microanalyse du CNRS, Lyon.

All reagents and supporting electrolytes were used as obtained commercially. Solvents were distilled according to usual procedures. Metals used as the anode were of high purity (Ventron, Alfa Produkte).

Synthesis of Dimethyl 1,2-Cyclopentanedicarboxylate (Typical Procedure). In a 50-mL cylindrical undivided glass cell fitted with an Al rod as the anode and a cylindrical stainless steel grid as the cathode were introduced NMP (40 mL), NBu_4BF_4 (0.1 g, 0.3 mmol), and NBu_4I (0.2 g, 0.54 mmol), as the supporting electrolyte, 1,3-dibromopropane (4 g, 20 mmol), and dimethyl maleate (1.44 g, 10 mmol). Three moles of electrons was passed per mole of dimethyl maleate, under argon, at constant current with a current density of 2 A/dm^2. The reaction mixture was then poured into a cold mixture of 1 N 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 $MgSO_4$, and evaporated. Flash chromatography on silica gel with 1/4 diethyl ether–pentane gave dimethyl 1,2-cyclopentanedicarboxylate[10] (0.81 g, yield 43%) as a mixture of two isomers in a 10/1 ratio as determined by gas chromatography and GC–MS analysis: ^{1}H NMR ($CDCl_3$, major isomer) 3.70 (s, 6 H), 3.13 (m, 2 H), 2.06 (m, 2 H), 1.83 (m, 2 H), 1.75 (m, 2 H); ^{13}C NMR ($CDCl_3$) 175.41 (s), 51.65 (q), 46.68 (d), 29.88 (t), 29.91 (t); GC–MS (m/z, relative intensity) major isomer 187 (37), 155 (15), 126 (67), 113 (29), 67 (100); GC–MS (m/z, relative intensity) minor isomer 187 (6), 155 (40), 126 (32), 113 (56), 67 (100). The identification of the major isomer was made as follows: 0.1 g of the purified mixture was refluxed in 1 N alcoholic NaOH (3 mL) for 12 h. The solution was then acidified to pH 5 with 1 M H_2SO_4 and extracted continuously with diethyl ether to give a white solid (0.07 g). Crystallization in water gave *trans*-1,2-cyclopentanedicarboxylic acid (0.04 g), mp(uncorrected) 160–161 °C (lit.[12] mp 162 °C).

Electrochemical Reactions in a Two-Compartment Cell in the Presence of Electrogenerated Aluminum Bromide. The cathode was a gold grid and the anode a stainless steel one. Both compartments were filled with NMP (30 mL) containing NBu_4I (2 g, 5.4 mmol) and NBu_4BF_4 (1 g, 3 mmol). In a first stage, the desired amount of $AlBr_3$ was formed in the cathodic compartment by reduction of $C_2H_4Br_2$ in the presence of an aluminum rod acting as the anode. The aluminum rod was then removed, and dimethyl maleate (1.44 g, 10 mmol) and 1,3-dibromopropane (4 g, 20 mmol) were introduced in the cathodic chamber. The divided cell was then properly connected to the dc power supply, providing a constant current with a current density of ca. 0.1 A/dm^2. Workup and analysis were performed as usual.

Identification of the Products. Methyl 5-(chloromethyl)-3-(methoxycarbonyl)-5-hexenoate (L2): ^{1}H NMR 5.22 (m, 1 H), 5.01 (m, 1 H), 4.07 (m, 2 H), 3.69 (s, 3 H), 3.68 (s, 3 H), 3.07 (m, 1 H), 2.60 (m, 4 H); ^{13}C NMR 174.80, 127.28, 142.05, 117.48, 51.97, 47.57, 39.59, 39.39; GC–MS (relative intensity) 205 (6.1), 204 (4.6), 203 (18.3), 202 (14), 199 (86.6), 176 (31.5), 174 (94), 139 (52.7), 107 (21.9), 79 (100), 59 (69); HRMS for $C_{10}H_{15}ClO_4$, calcd 234.0658, found 234.0665.

The following products were characterized by comparison of their GC and spectral data with those for commercially available samples: methyl cyclopentanecarboxylate (**C6**); phenylcyclohexane (**C7**); methyl 5-hexenoate (**L6**); *trans*-dimethyl 1,2-cyclohexanedicarboxylate (**C12**); *trans*-dimethyl 4-cyclohexene-1,2-dicarboxylate (**C13**); *trans*-dimethyl 1,2-cyclopropanedicarboxylate (**C8**); *trans*-methyl 2-phenylcyclopropanecarboxylate (**C9**).

The following compounds were identified by comparison of their physical and spectral data with those given in the cited references: *trans*-dimethyl 4-methylene-1,2-cyclopentanedicarboxylate (**C2**);[13] *trans*-methyl 2-phenylcyclopentanecarboxylate (**C4**);[14] methyl 1-phenylcyclopentanecarboxylate (**C5**);[15] 2-phenylcyclopentyl methyl ketone (**C3**);[16] methyl 3-(methoxycarbonyl)-5-hexenoate (**L1**);[17] methyl 3-phenyl-5-hexenoate (**L4**).[17]

Acknowledgment. We thank Dr. J. Zylber for his assistance in preparation of the manuscript.

Registry No. **C1**, 941-75-3; **C2**, 37575-81-8; **C3**, 109583-32-6; **C4**, 37108-10-4; **C5**, 4535-96-0; **C6**, 4630-80-2; **C7**, 700-88-9; **C8**, 826-35-7; **C9**, 5861-31-4; **C11**, 7371-67-7; **C12**, 3205-35-4; **C13**, 17673-68-6; **L1**, 1069-40-5; **L2**, 125715-34-6; **L4**, 52129-50-7; **L6**, 2396-80-7; NMP, 872-50-4; HMPT, 680-31-9; DMF, 68-12-2; THF, 109-99-9; TMU, 632-22-4; *cis*-$MeO_2CCH{=}CHCO_2Me$, 624-48-6; *trans*-$MeO_2CCH{=}CHCO_2Me$, 624-49-7; *trans*-$PhCH{=}CHCOCH_3$, 1896-62-4; *trans*-$PhCH{=}CHCO_2Me$, 1754-62-7; $CH_2{=}C(Ph)CO_2Me$, 1865-29-8; $CH_2{=}CHCO_2Me$, 96-33-3; CH_2Br_2, 74-95-3; $ClCH_2CH_2Cl$, 1300-21-6; $Br(CH_2)_3Br$, 109-64-8; $CH_2{=}C(CH_2Cl)_2$, 1871-57-4; $Br(CH_2)_4Br$, 110-52-1; *cis*-$ClCH_2CH{=}CHCH_2Cl$, 1476-11-5; CH_2Cl_2, 75-09-2; $PhCHCl_2$, 98-87-3; NBu_4BF_4, 429-42-5; NBu_4I, 311-28-4; NBu_4Br, 1643-19-2; LiCl, 7447-41-8; Al, 7429-90-5; Mg, 7439-95-4; stainless steel, 12597-68-1.

---

(12) Wasserman, A. *Helv. Chim. Acta* **1930**, *13*, 207.

(13) Trost, B. M.; Chan, M. T. *J. Org. Chem.* **1983**, *105*, 2315.

(14) Bordwell, F. G.; Strong, J. G. *J. Org. Chem.* **1973**, *38*, 579.

(15) Gonzenbach, H. U.; Tegmo-Larsson, I. M.; Crosclaude, J. P.; Schaffner, K. *Helv. Chim. Acta* **1977**, *60*, 109.

(16) Brown, H. C.; Srebnick, M.; Bakshi, R. K.; Cole, T. E. *J. Am. Chem. Soc.* **1987**, *109*, 5420.

(17) Majetich, G.; Casares, A. M.; Chapman, D.; Behnke, M. *Tetrahedron Lett.* **1983**, *24*, 1909.