

## Mn(III)-Mediated Electrochemical C,C-Bond Formation : Radical Addition of Polyhalomethanes to Olefins

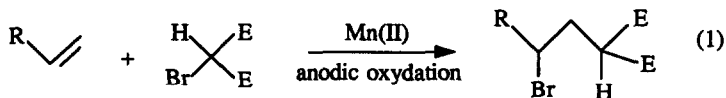
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**Key Words** : Radical addition reactions; Manganic salt; Electrochemistry

**Abstract** : Free-radical chain addition of various polyhalomethanes onto olefins can be easily initiated by electrochemically *in situ* generated manganic salt used in catalytic amount associated with an equimolar amount of a Mn(III)-oxidizable compound like methyl cyano- or aceto-acetate.

*In-cell* electrochemical regeneration of oxidative or reductive metallic complexes turning into catalytic a stoichiometric reaction is quite promising in regard to both development and environment accounts.<sup>1</sup> This was illustrated recently by two reported studies on the Mn(III)-promoted electrochemical addition of active methylene compounds to olefins, one dealing with the synthesis of sorbic acid precursors,<sup>2</sup> the other with the addition of alkyl cyano- or aceto-acetate, or dialkyl malonate to cyclic and terminal olefins.<sup>3</sup> Intermediacy of radicals has been suggested mainly on the basis of literature data,<sup>4</sup> but no chain mechanism appears to be involved in these reactions inasmuch as a near stoichiometric amount of electricity was required.<sup>2,3</sup>

We quite recently described another approach<sup>5</sup> combining the electrocatalyzed Mn(III)-generation of free radicals with an efficient radical addition reaction, i.e. the addition of dialkyl bromomalonate to olefins (eq 1).



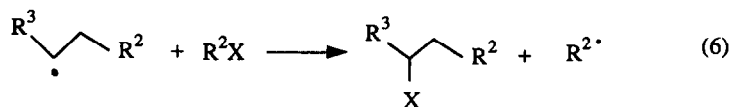
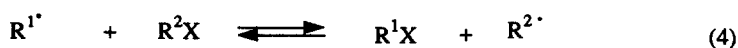
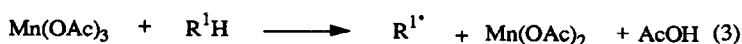
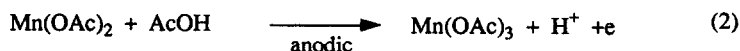
Dialkyl bromomalonate can indeed both be readily oxidized by Mn(III) into a free radical and lead to an efficient bromine transfer reaction in the propagation process.<sup>5</sup>

It then became highly desirable to extend this method to the addition of other reagents notably polyhalomethanes such as CBr<sub>4</sub>, BrCCl<sub>3</sub>, CF<sub>2</sub>Br<sub>2</sub>, or dialkyl dibromomalonate. Since these are not enolizable compounds, they can not be oxidized by Mn(III). We have overcome this limitation by adding to the reaction mixture a small amount of a Mn(III)-oxidizable compound which would be involved in the initiation of the chain addition. Convenient compounds to play this role are active methylene compounds such as methyl cyano- or aceto-acetate, or 1,5-pentadione.

This approach has proved to be successful in the typical addition reactions indicated in the table. The reactions were conducted under the following experimental conditions : a solution of  $\text{Mn}(\text{OAc})_2$  (2 mmol), methyl cyanoacetate (2 mmol), the halide (20 mmol), and the olefin (40 mmol) in AcOH (40 ml) containing AcOK (20 mmol) was electrolyzed under constant current intensity ( $I = 0.1 \text{ A}$ ) in a undivided beaker-type cell having two concentric electrodes made of carbon fiber (anode) and stainless steel (cathode). Reaction temperature and electricity consumption are given in the table.


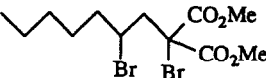

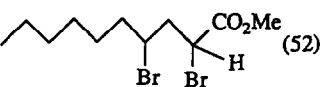

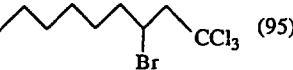

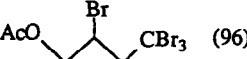

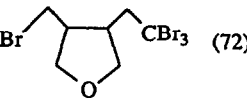

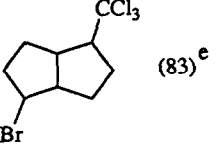
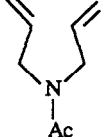
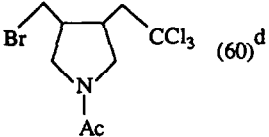

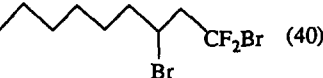

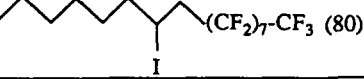
The expected adducts were obtained with high chemical and faradaic yields. The nature of the adducts is in keeping with a free-radical chain addition reaction. Notably the formation of cyclic products by addition of  $\text{CBr}_4$  to diallylether (table, entry 5) or of  $\text{BrCCl}_3$  to 1,5-cyclooctadiene (table, entry 6) or to N-acetyl-N,N-diallylamine (table, entry 7) is highly consistent with the intermediacy of radicals.

The process can be described according to the following mechanism where  $\text{R}^1\text{H}$  and  $\text{R}^2\text{X}$  stand for respectively the active methylene compound and the halocompound, the cathodic reaction being the reduction of protons :



In the absence of either the Mn salt or the active methylene compound, or both no more than 15 % of the adduct was formed after 1 F/mol of halide was passed. We found that the anode potential was at least 1 V higher than when  $\text{Mn}(\text{OAc})_2$  was present (1V vs SCE) indicating that a Kolbe reaction could occur thus generating radicals, though not very efficiently. We also checked that the cathodic reaction was always the reduction of  $\text{H}^+$ , that is to say that no electroreduction of the halide, first leading to anions which would then, due to the absence of a membrane, be oxidized into radicals occurs as the key reaction.

Table Mn(III)-Promoted Addition of Organic gem-Dihalides to Olefins<sup>a</sup>

Entry	Halide	Olefin	Product (Yield %) <sup>b</sup>	Electricity (F/mol)
1	Br <sub>2</sub> C(CO <sub>2</sub> Me) <sub>2</sub>		 (61)	0.06
2	Br <sub>2</sub> CHCO <sub>2</sub> Me		 (52)	0,15
3	BrCCl <sub>3</sub>		 (95)	0,1
4	CBr <sub>4</sub>		 (96)	0.1
5	CBr <sub>4</sub>		 (72) <sup>d</sup>	0.05
6	BrCCl <sub>3</sub>		 (83) <sup>e</sup>	0.6
7	BrCCl <sub>3</sub>		 (60) <sup>d</sup>	0.6
8	CF <sub>2</sub> Br <sub>2</sub> <sup>c</sup>		 (40)	0.17
9	C <sub>8</sub> F <sub>17</sub> I <sup>c</sup>		 (80)	0.1

<sup>a</sup> AcOH(40 ml), AcOK (2 g), halide (20 mmol), Mn(OAc)<sub>2</sub> (0.2 g), methyl cyanoacetate (0.17 ml, 2 mmol) olefin (40 mmol), halide (20 mmol), I = 0.1 A, undivided cell, 40 °C. <sup>b</sup> based on isolated product. <sup>c</sup> room temperature. <sup>d</sup> mixture of cis:trans = 4.5. <sup>e</sup> cis junction

The free-radical addition of *gem*-polyhalomethanes has been performed with various initiators such as peroxydes, azo-bis-isobutyronitrile, light, or redox systems.<sup>6</sup> Our approach offers an interesting alternate methodology to run such radical addition reactions at or near room temperature, which is of special interest in the use of volatile reagents (e.g. CF<sub>2</sub>Br<sub>2</sub>), and with an easy control of the initiation by simply adjusting the current intensity.

## References

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