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Publisher *Taylor & Francis*

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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Electrochemical Generation of Diisopropyl 1,1 - Dichloromethylphosphonate Anion. Application to an Efficient Synthesis of Various Cycloalkylphosphonates

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To cite this Article Jubault, Philippe , Feasson, Christian and Collignon, Noel(1996) 'Electrochemical Generation of Diisopropyl 1,1 -Dichloromethylphosphonate Anion. Application to an Efficient Synthesis of Various Cycloalkylphosphonates', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 111: 1, 118

To link to this Article: DOI: 10.1080/10426509608054747

URL: <http://dx.doi.org/10.1080/10426509608054747>

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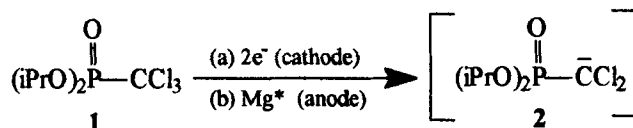
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ELECTROCHEMICAL GENERATION OF DIISOPROPYL 1,1-DICHLOROMETHYLPHOSPHONATE ANION. APPLICATION TO AN EFFICIENT SYNTHESIS OF VARIOUS CYCLOALKYLPHOSPHONATES

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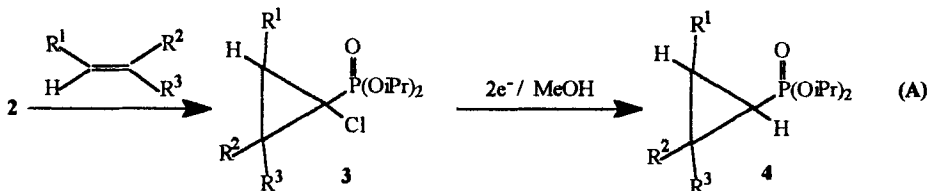
Key Words: Cycloalkylphosphonates, Electrosynthesis, Electrochemical activation of magnesium.

The electrochemical reduction of phosphonate **1**, in DMF, in a one-compartment electrolysis cell equipped with a felt carbon cathode and a sacrificial anode of magnesium gave the carbanion **2** according to an unusual mechanism, involving two simultaneous phenomena: (a) a bielectronic process at the cathode, (b) a direct reduction of phosphonate **1** by the magnesium rod, activated on its surface by the anodic process:

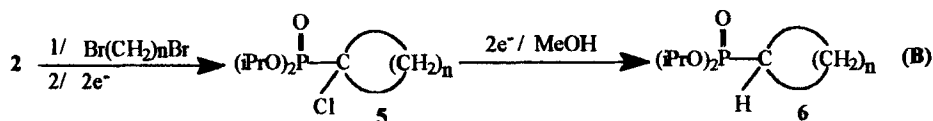


The electrogenerated carbanion **2** was reacted:

(A) with Michael acceptors giving α -chloro cyclopropylphosphonates **3** (64-85 % yield):



(B) with ω,ω -dibromoalkanes leading to monoalkylated intermediates, which after electrochemical reduction, followed by cyclisation gave α -chloro cycloalkylphosphonates **5** (64 - 72 % yield):



Moreover, the further electrochemical reduction of **3** or **5** in the presence of a protic agent, led to cycloalkylphosphonates **4** or **6** respectively, in a one-pot operation starting from **1** (50 - 58 % overall yield).