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CATHODIC FORMATION OF OLEFINS FROM PHOSPHONATES[1)]

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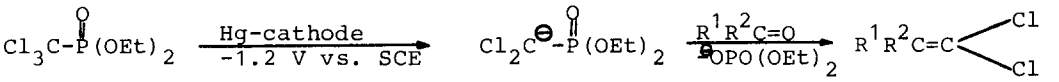
Cathodic reduction of diethyl trichloromethylphosphonate in the presence of carbonyl compounds yields in a Horner-Emmons reaction, 1,1-dichloroalkenes. Similarly triethyl phosphonodichloroacetate affords α-chloro-α,β-unsaturated esters.

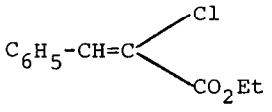
Phosphonate carbanions are frequently employed organophosphorus compounds for olefin synthesis[2)]. We found that the diethyl dichloromethylphosphonate anion 2 can be generated cathodically from diethyl trichloromethylphosphonate (1) and reacted with carbonyl compounds to afford 1,1-dichloroalkenes 3. (Table)



1 2 3

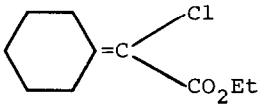
Compared to the generation of 2 with n-butyllithium[3)] the electrolytic method has the advantage that it avoids the strongly basic and expensive lithium alkyls[4)].

Similarly triethyl phosphonodichloroacetate[5)] can be reduced in the presence of benzaldehyde or cyclohexanone to yield the α-chloro-α,β-unsaturated esters 4 and 5.



55 %, E/Z = 40/60

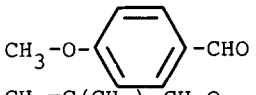
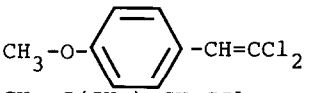
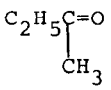
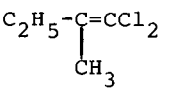
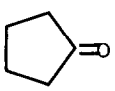
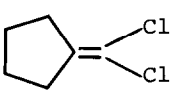
4



43 %

5

Table: Dichloroalkenes by cathodic reduction of diethyl trichloromethylphosphonate in the presence of carbonyl compounds.

carbonyl compound	dichloroalkene	yield[a]
		40 %
$CH_2=C(CH_3)-CH=O$	$CH_2=C(CH_3)-CH=CCl_2$	45 %
		39 %
$CH_3(CH_2)_4CH=O$	$CH_3(CH_2)_4CH=CCl_2$	30 %
$(C_4H_9)_2C=O$	$(C_4H_9)_2C=CCl_2$	24 %
		52 %

a) Isolated yield based on current consumption; all compounds are characterized by ^{1}H-NMR, IR, MS and elemental analysis.

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