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α-CHLORO-α,β-UNSATURATED ESTERS FROM DIETHYL 2,2-DICHLORO-1-ETHOXYVINYL PHOSPHATE

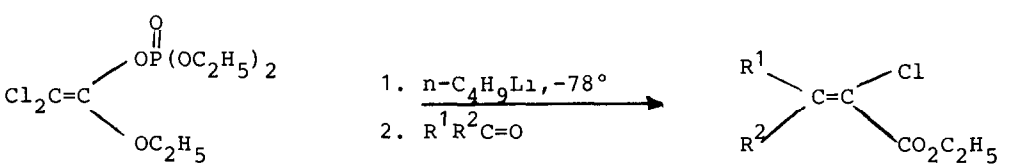
F. Karrenbrock and H.J. Schäfer

Organisch-Chemisches Institut der Universität Münster

Orléans-Ring 23, D-4400 Münster, West Germany

Diethyl 2,2-dichloro-1-ethoxyvinyl phosphate obtained by Perkow reaction from ethyl trichloroacetate and triethyl phosphite affords with carbonyl compounds after lithiation α-chloro-α,β-unsaturated esters.

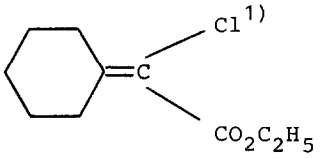
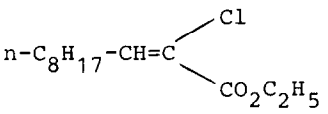
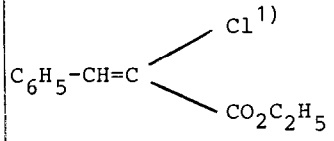
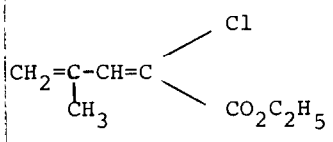
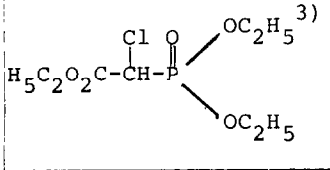
Villieras[1] recently described the synthesis of α-chloro-α,β-unsaturated esters (2) by reacting carbonyl compounds with *in situ* generated diethyl 1-chloro-1-ethoxycarbonyl-1-lithiomethane phosphonate. We found that the unsaturated esters 2 can be prepared alternatively by lithiation of diethyl 2,2-dichloro-1-ethoxyvinyl phosphate (1) and reaction with aldehydes and ketones (Scheme, Table)



1 2

1 can be prepared in 83 % yield from ethyl trichloroacetate and triethyl phosphite[2].

Table: α-Chloro-α,β-unsaturated esters from diethyl 2,2-dichloro-1-ethoxyvinyl phosphate.

Carbonyl compound	product[a]		yield[b]	E/Z-ratio[c]
Cyclohexanone		3	78 %	-
Nonanal[d]		4	55 %	E/Z = 42/58
Benzaldehyde		5	85 %	E/Z = 47/53
2-Methyl-2-propenal		6	50 %	E/Z = 34/66
Hydrolysis with 2 N HCl		7	68 %	-

a) The structures 3 - 7 were characterized by their IR-, ^{1}H-NMR- and mass spectra. b) Isolated yield calculated on 1. c) The E/Z-ratio was determined by G.L.C. analysis from the crude product. d) Before addition of the carbonyl compound 1 - 2 ml hexamethyl-phosphorous triamide were added to the reaction mixture.

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2) F. W. Lichtentaler, Chem. Rev. 61, 607 (1961).
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