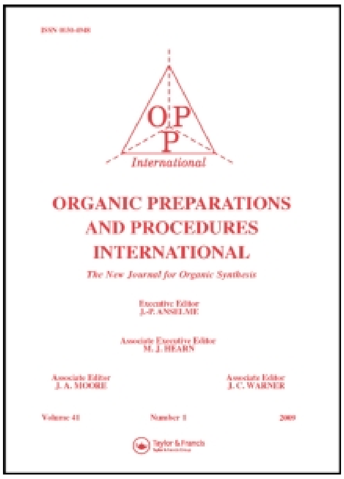

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CONVENIENT ONE-POT PROCESSES FOR THE PREPARATION OF CHLOROACETALDEHYDE DIALKYL ACETALS

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CONVENIENT ONE-POT PROCESSES FOR THE PREPARATION OF CHLOROACETALDEHYDE DIALKYL ACETALS

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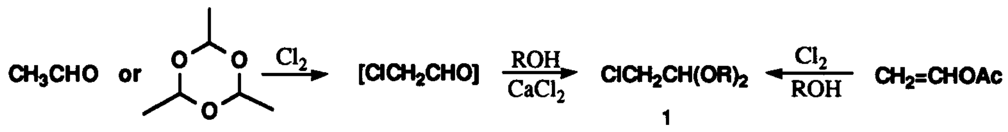
Chloroacetaldehyde dialkyl acetals are versatile intermediates in the synthesis of compounds of biological significance. The commonly used methods for their preparation involve the alcoholysis of 1,2-dichloro-1-alkoxyethanes,[1] chlorine addition and alcoholysis of vinyl chloride[2] or vinyl alkyl ethers,[3] addition of alkoxy halides to vinyl alkyl ethers,[4] acetalization of chloroacetaldehyde,[5] chlorination of ethanol,[6] and electrolysis of ethanol and hydrogen chloride.[7] The starting material used in all these methods either require a multistep process for their production or rigorous experimental conditions for their conversion to title products. This communication reports two convenient and rapid one-pot processes for the preparation of these compounds by chlorination of acetaldehyde[8] (or paraldehyde) or of vinyl acetate[9] and subsequent *in situ* acetalization of the generated chloracetaldehyde or 1,2-dichloroethyl acetate respectively with simple unbranched alcohols. These processes seem to be advantageous as the reaction times are shorter and overall yields are better when compared to other methods.



a) R = Me b) R = Et c) R = n-Pr

EXPERIMENTAL SECTION

The purity of the products was determined by GLC using Aimil-Nucon gas chromatograph series 5500 fitted with a 3% SE-30 column under usual operating parameters (detector-FID, column length: 3 meters, column width 2 mm, carrier gas: nitrogen, fuel gas: hydrogen, flow rate of carrier gas: 40 ml/min, injection temperature: 220°, column temperature: 180° and detection temperature: 230°). Analytical samples were prepared by two distillations *in vacuo*. The identity of the compounds were supported by direct comparison of IR spectra with those of authentic samples.

Chloroacetaldehyde Dialkylacetals

1. From Acetaldehyde or Paraldehyde. General Procedure.- A gentle stream of chlorine gas was absorbed in neat acetaldehyde (3-6 moles) or paraldehyde (1-2 moles) in 1 L three-neck flask fitted with a mechanical stirrer until 2.2 fold increase in weight was observed. Stoichiometric quantities of anhydrous calcium chloride and of the alcohol were added at 20-30° and the reaction mixture was stirred for 4 hrs. Upon addition of water, an oily product separated and was distilled to yield chloroacetaldehyde dialkylacetal (**1**) of 99% purity.

2. From Vinyl Acetate. General Procedure.- A gentle stream of chlorine was passed through a solution of vinyl acetate (43.0 g, 0.5 mol) in desired alcohol (methanol. ethanol or *n*-propanol) (1.6 mol) in a three-neck flask fitted with a mechanical stirrer 1-4° until the weight of the reaction mixture increased by 35.5 g (0.5 mol of chlorine). This took approximately 2 hrs. The reaction mixture was allowed to come to room temperature and unreacted alcohol was removed by distillation on steam bath. The residual brownish oily product was distilled *in vacuo* to yield the desired chloroacetaldehyde dialkyl acetal of 99% purity.

Both reactions should be carried out in a well-ventilated hood.

TABLE 1. Chloroacetaldehyde Dialkylacetals from Acetaldehyde and Vinyl Acetate

Cmpd	Yield(%)[a] 1	Yield(%)[a] 2	bp.[b] (°C)/mm Hg.	lit. data
1a	50	64	77-80/190	57/49[3]
1b	48	64	85-89/70	70-71/35[3]
1c	45	64	84-85/50	81/20[3]

a) Method 1: from acetaldehyde; Method 2: from vinyl acetate b) Boiling points are uncorrected.

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