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STABLE DIALKOXYMETHYL HALOGENIDES

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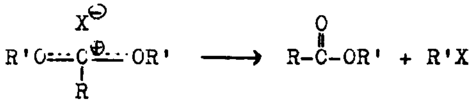
During the last decades several investigators[1,2,3,4,5,6,7] have tried to isolate cyclic and non-cyclic dialkoxyalkyl chlorides ($RC(OR')_2Cl$). Although the presence of these compounds as reaction intermediates was often evident isolation was impossible on account of their high instability. In recent investigations[8] the presence of 2-chloro-2-dichloromethyl-1, 3-dioxolan in a reaction mixture at -60° could be shown by N.M.R.-measurements. This urges us to publish the first synthesis and isolation of diethoxymethyl fluoride and dineopentoxymethyl chloride.

The dialkoxyalkyl halogenides will have reasonable carboxoniumion character[9] and decomposition will probably occur by nucleophilic attack of X^- on the ∝ -carbon atom in R' which directs the reaction irreversibly in the thermodynamically favoured way[4] according to



$$R'O\overset{X^{\ominus}}{\underset{R}{\overset{\vert}{C}}}{}^{\oplus}OR' \longrightarrow R-\overset{O}{\overset{\Vert}{C}}-OR' + R'X$$

Stability can be increased by making substitution on the ∝ -carbon atom difficult, giving the dialkoxymethylgroup less carboxonoiumion character and/or making X^- less nucleophilic. This explains why diphenoxymethyl chloride[10,11] and 1,1 divinyloxy-1-chloroethane[12] were stable enough to be isolated. So it can also be predicted that the stability of dialkoxymethyl halogenides decreases in the sequence X = F, Cl, Br. An analogous decreasing stability was already found for the compounds $HC(OC_2H_5)_2X$[13,14] in the sequence X = phenoxy, p-nitrophenoxy, 2,4-dinitrophenoxy, and in the sequence X = acetate, formate, chloroacetate.

The diethoxymethyl fluoride could be synthesized from diethoxymethyl butyrate[13] and KHF_2 according to

$HC(OEt)_2OCO\underline{n}\text{-}Prop + KHF_2 \longrightarrow HC(OEt)_2F + KF + HOCO\underline{n}\text{-}Prop$

It was evaporated from the reaction mixture at 20 mm pressure and condensed at low temperature. The fluoride is stable up to $\sim 40^{\circ}$.

Dineopentoxymethyl chloride was obtained from trineopentoxymethane and acetyl chloride.

$HC(ONeopent)_3 + MeCOOl \longrightarrow HC(ONeopent)_2Cl + NeopentOCOMe$

Both compounds are very reactive to water and other nucleophilic compounds. When added to a suspension of sodium methanolate in ether mixed orthoformates or their disproportionation products were isolated. Structures were determined from N.M.R.-spectra and by determination of the saponification equivalents according to

$HO(OR)_2X + 2NaOH \longrightarrow NaX + NaOCOH + 2ROH$

Apart from their reactivities with nucleophiles and their activities as halogenating agents dialkoxy-methyl halogenides may be an interesting source for dialkoxy carbenes.

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