LEWIS ACID CATALYZED ADDITIONS TO METHYL OLEATE

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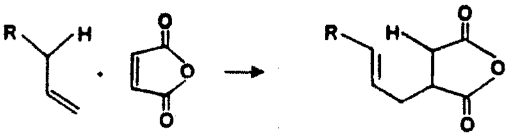
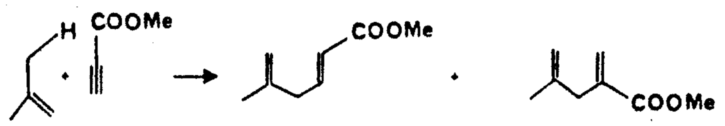
INTRODUCTION

The reaction of an alkene having an allylic hydrogen ("ene") with a compound containing a double or triple bond ("enophile") to form a new bond with migration of the ene double bond and 1,5-hydrogen shift is referred to as the ene reaction[1-3], e.g. the ene reaction of an alkene with maleic anhydride.

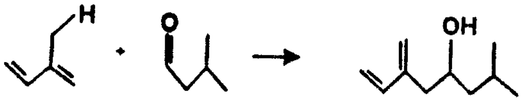


The reaction is carried out under thermal conditions or by use of Lewis acids such as $SnCl_4$, $AlCl_3$, $(CH_3)_2AlCl$, $EtAlCl_2$ as catalysts[2]. The catalyzed ene reaction occurs at room temperature with a higher selectivity than the thermal ene reaction[2].



Thermal:	200°	47%	3%
$AlCl_3$:	25°	61%	-

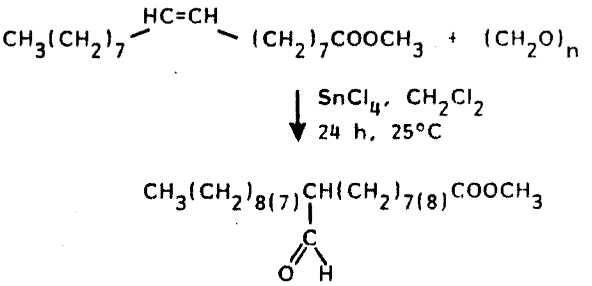
Aldehydes have been used extensively as enophiles in Lewis acid catalyzed ene reactions[2,4], e.g. the $(CH_3)_2AlCl$ - catalyzed ene reaction of isoprene and isobutyraldehyde[2].



$(CH_3)_2AlCl$ catalyzes the ene reaction of formaldehyde with all types of alkenes[5]. Formaldehyde undergoes BF_3- or $SnCl_4$ - catalyzed reactions with 1,1-di- or tri-substituted ethylenes[6].

$SnCL_4$-CATALYZED ADDITION OF PARAFORMALDEHYDE TO METHYL OLEATE.

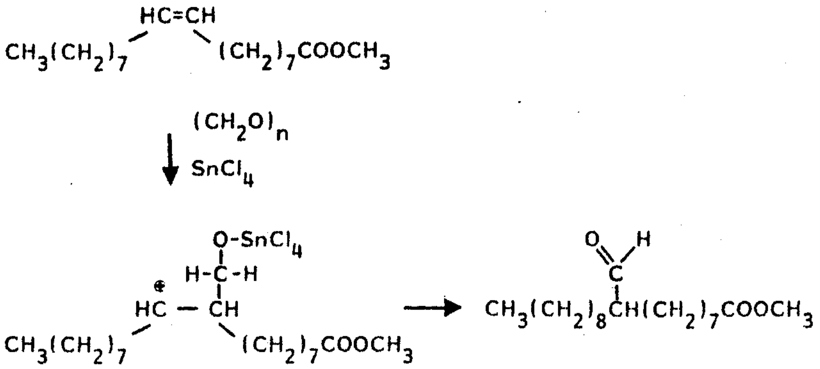
We are interested in the application of the ene reaction to unsaturated oleochemicals[3] and examined the possibility of $SnCl_4$ - catalyzed addition of paraformaldehyde to methyl oleate at room temperature. The reaction product we obtained was not the expected ene product. The reaction afforded in good yield (75 %) the methyl 9(10)-formylstearate.



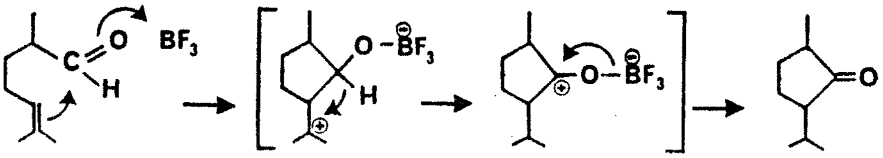
$$CH_3(CH_2)_7\overset{HC=CH}{\diagup\quad\diagdown}(CH_2)_7COOCH_3 + (CH_2O)_n \xrightarrow[24\ h,\ 25^\circ C]{SnCl_4,\ CH_2Cl_2} CH_3(CH_2)_{8(7)}\underset{\underset{O\diagup\diagdown H}{C}}{CH}(CH_2)_{7(8)}COOCH_3$$

Methyl oleate : paraformaldehyde : $SnCl_4$ = 1 : 1 : 1

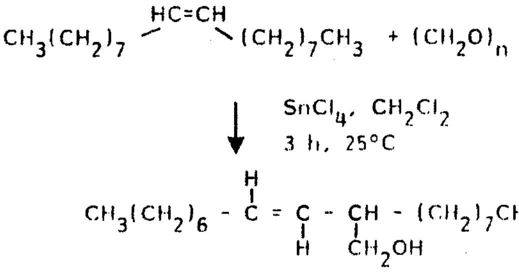
It is suggested that this product results from an electrophilic additon of the formaldehyde - $SnCl_4$-complex to the double bond of the methyl oleate. The zwitterionic intermediate rearranges by a hydride shift to give the methyl formyl-stearate.



Lewis-acid catalyzed intramolecular additions of aldehydes to the C,C-double bond to give a cyclic ketone have been described[7,8].



The carboxymethyl group of the methyl oleate seems to play an important role in the reaction because the $SnCl_4$-catalyzed reaction of Z-9-octadecene with paraformaldehyde affords the expected ene product E-2-octyl-3-undecenol.

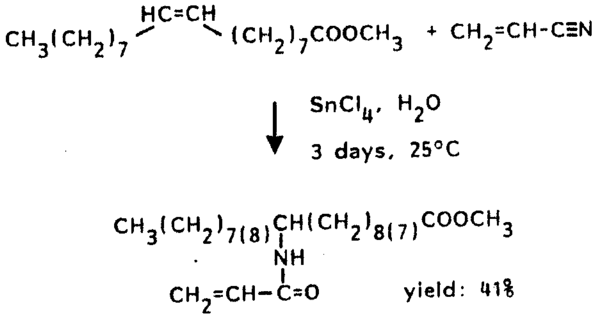


yield: 55%

Z-9-octadecene : paraformaldehyde : $SnCl_4$ = 1 : 1 : 1

$SnCl_4$-CATALYZED ADDITION OF ACRYLONITRILE TO METHYL OLEATE.

Tin(IV)chloride catalyzes the addition of acrylonitrile to methyl oleate at room temperature in a slow reaction. The reaction that takes place is not the expected ene reaction but a Ritter-reaction[9] and the resulting product is methyl (N-acryl)-9(10)-amino-stearate.



$$CH_3(CH_2)_7\overset{HC=CH}{\diagup\quad\diagdown}(CH_2)_7COOCH_3 + CH_2=CH-C\equiv N \xrightarrow[\text{3 days, 25°C}]{SnCl_4,\ H_2O} CH_3(CH_2)_{7(8)}\underset{\underset{CH_2=CH-\overset{|}{C}=O}{\overset{|}{NH}}}{CH}(CH_2)_{8(7)}COOCH_3$$

yield: 41%

The addition of acetonitrile to methyl oleate was carried out as well and afforded methyl (N-acetyl)-9(10)-amino-stearate.

Roe and Swern[10] describe the Ritter-reaction of oleic acid with nitriles e.g. acetonitrile in 95% sulfuric acid solution to give N-acetyl-amino-stearic acid in good yield. In sulfuric acid, however, considerable isomerization occurs.

It is of interest that under conditions of $SnCl_4$-catalysis migration of the double bond has not been observed. Acrylonitrile is added to C9 or C10 of methyl oleate. Hydrolysis of the adduct with methanolic potassium hydroxide affords the methyl 9(10)-amino-stearate.

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