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PREPARATION AND INVESTIGATION OF TRIALKOXY-SILYL DERIVATIVES OF SATURATED CARBOXYLIC ACIDS

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Abstract

A study was carried out on the preparation of triethoxy-silyl derivatives of the allyl esters of several carboxylic acids. This has been achieved by the preparation of the allyl esters of carboxylic acids followed by the addition of triethoxy-silane, $HSi(OCH_2CH_3)_3$ on the double bond of the allyl group. The new compounds were characterized by refractivity, density, boiling point, elemental analysis, IR and ^{1}H-NMR spectroscopy methods.

Keywords: trialkoxy-silyl derivatives, hydrosilylation, coupling agent, surface treatment.

1. Introduction

The hydrosilylation of carboxylic acid allyl esters with trialkoxy-silanes has been studied extensively because of the potential application of these compounds as coupling agents.

The allyl esters of α,β-unsaturated acids, such as acrylic acid and methacrylic acid readily undergo hydrosilylation reaction with triethoxy-silane in the presence of $H_2[PtCl_6]PhCOOMe$ [1]; $H_2[PtCl_6]$ [cyclohexanone], $[CH_2 = CH\text{-}Si(OEt)_3]$; $Pt[CH_2 = CH_2][PPh_3]_2$ [2], forming 3-(triethoxy-silyl)-propyl-acrylate or in the case of only $H_2[PtCl_6]$ [3] or $H_2[PtCl_6](2-Pr-OH)+CH_2 = CH-O-Bu$ [4] or $PtCl_2$ [acetyl-acetonate]$_2$ [5] the corresponding methacrylate derivative can be prepared in good yield.

It is typical of these reactions that the addition of hydrosilane occurs on the allyl double bond resulting a β-adduct. (Both the C=C bond in the acrylic and the C=O in the carbonyl group remain untouched.) 3-(methacryloxy)-propyl-triethoxy-silane is a well-known product for surface-treatment of glass fibers reinforcing unsaturated polyester resins [6].

The hydrosilylation of the allyl esters of unsubstituted or substituted saturated carboxylic acids occurs with $H_2[PtCl_6](2 - Pr - OH)$ also called Speier's catalyst or with γ-Al_2O_3-supported Pt metal selectively at the

C=C double bond giving β-adduct in accordance with the Farmer's rule [7]. A great number of compounds of this class have been prepared, e.g. the hydrosilyl derivatives ($HSiX_3$, where $X = -Cl, -OCH_3, -OCH_2CH_3$) of allyl chlorformate [8], allyl carbonate [9], allyl acetate [10,11] and the α-substituted form of the following compound [12]:

$$YCH_2COO - CH_2CH_2CH_2 - SiCl_3 \ ,$$

where

$$Y = H, \quad C_6H_5O-, \quad Cl-, \quad CH_3O-, \quad C_2H_5O-, \quad n - C_3H_7O - \ .$$

These reactions are very often accompanied by several side-reactions [13]:

$$R^1COOCH_2CH = CH_2 + HSiR_nCl_{3-n} \xrightarrow{Pt/Al_2O_3 \text{ or } H_2[PtCl_6]}$$

$$\underset{\text{main product}}{R^1COOCH_2CH_2CH_2SiR_nCl_{3-n}} + \underset{\text{by product}}{CH_3CH = CH_2} + \underset{\text{by-product}}{R^1COO - SiR_nCl_{3-n}} \text{ etc.}$$

where

$$R = CH_3-, C_2H_5-, C_2H_5O - \ .$$

Our study is focused on the preparation of 3-(triethoxy-silyl)-propyl esters of acetic acid [11,14,15] and of acids of longer alkyl chains: pelargonic acid and stearic acid. The further aim of this work was to use these substrates as coupling agents for $CaCO_3$ and other clay minerals as fillers of polyolefines. This part of the work is beyond the scope of this paper.

2. Experimental

2.1. Synthesis of 3-(Triethoxy-Silyl)-Propyl Acetate, Pelargonate and Stearate

These products were synthesized according to the following reaction scheme:

3-(triethoxy-silyl)-propyl acetate, TESPA

$$CH_3COOH + CH_2 = CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3COOCH_2CH = CH_2 \qquad (1)$$

$$CH_3COOCH_2CH{=}CH_2 + HSiOC_2H_5)_3 \xrightarrow{H_2[PtCl_6]+2-PrOH} CH_3COO(CH_2)_3SiOC_2H_5)_3 \quad (2)$$

TESPA

3-(triethoxy-silyl)-propyl pelargonate, TESPP

$$CH_3(CH_2)_7COOH + CH_2{=}CHCH_2OH \xrightarrow{\text{p-toluyl-sulphonic acid in benzene}} CH_3(CH_2)_7COOCH_2CH = CH_2 \quad (3)$$

$$CH_3(CH_2)_7COOCH_2CH{=}CH_2 + HSi(OC_2H_5)_3 \xrightarrow{H_2[PtCl_6]+2-PrOH} CH_3(CH_2)_7COO(CH_2)_3Si(OC_2H_5)_3 \quad (4)$$

TESPP

3-(triethoxy-silyl)-propyl stearate, TESPS

$$CH_3(CH_2)_{16}COOH + CH_2{=}CHCH_2OH \xrightarrow{\text{p-toluyl-sulphonic acid in benzene}} CH_3(CH_2)_{16}COOCH_2CH{=}CH_2 \quad (5)$$

$$CH_3(CH_2)_{16}COOCH_2CH{=}CH_2 + HSi(OC_2H_5)_3 \xrightarrow{H_2[PtCl_6]+2-PrOH} CH_3(CH_2)_{16}COO(CH_2)_3Si(OC_2H_5)_3 \quad (6)$$

TESPS

2.1.1 Preparation of the Allyl Esters

2.1.1.1 Preparation of allyl acetate (Eq. (1)) [16]

Into a three-necked flask fitted with a Marcuson attachment along with a reflux condenser, 3.67 moles of freshly distilled allyl alcohol, 10.5 moles of 96% acetic acid and 5 ml cc. H_2SO_4 were poured and brought to the boil. Reaction time: 16 hours. The reaction mixture was neutralised with Na_2CO_3, separated and the aqueous phase was washed with diethyl ether. Both the ether and the organic phase were left over Na_2SO_4 (sicc) for two days. The two phases were poured together and distilled at 104 °C/0.1 MPa.
Yield: 76%, observed $nd^{20^\circ} = 1.4025$.
Literature data: bp.: 104 °C/0.1 MPa; $nd^{20^\circ} = 1.4045$ [16].

2.1.1.2 Preparation of allyl pelargonate (Eq. (3)) [17]

Into a flask of the arrangement described in 2.1.1.1 3.72 moles of allyl alcohol, 2.33 moles of pelargonic acid, 22 g of p-toluyl-sulphonic acid and 500 ml of benzene were poured. The solution was heated to the boiling point. The water formed during the reaction was azeotropically removed. Reaction time: 16 hours. The solution was distilled:
149 °C/0.0066 MPa. Yield: 84%, observed $nd^{20^\circ} = 1.4300$.
Literature data [17]: bp. : 151 °C/0.0066 MPa; $nd^{20^\circ} = 1.4302$, yield 85%.

2.1.1.3 Preparation of allyl stearate (Eq. (5)) [17]

In a flask of the same arrangement described in 2.1.1.1 3.67 moles of allyl alcohol, 2.29 moles of stearic acid, 21.78 g of p-toluyl-sulphonic acid and 500 ml of benzene were placed. The solution was refluxed for 16 hours and then left in the flask to cool down to room temperature. The content of the flask was filtered off and allowed to dry in air. The brownish material was recrystallised three times from acetone. Snow-white fatty-like crystals were gained.
Yield: 612.8 g, 82%. mp.: 36.5 °C; observed $nd^{40^\circ} = 1.4415$.
Literature data [17]: yield: 85%; mp.: 37.1 – 37.3 °C; $nd^{40^\circ} = 1.4420$.

2.1.2 Hydrosilylation Reaction of Allyl Esters with $HSi(OC_2H_5)_3$

0.1 mole/l hexachloro-platinic acid in 2-propyl alcohol, $H_2[PtCl_6]\cdot 6H_2O+2$-PrOH was used as a catalyst in the hydrosilylation reactions. The catalyst to triethoxy-silane molar ratio was as follows:

$$1 \text{ mole } HSi(OC_2H_5)_3 : 5 \cdot 10^{-5} \text{mole } H_2[PtCl_6] \cdot 6H_2O$$

2.1.2.1 Preparation of 3-(triethoxy-silyl)-propyl acetate, TESPA, (Eq. (2))

A mixture of 1.31 moles of allyl acetate, 1.31 moles of $HSi(OC_2H_5)_3$ was prepared. In a three-necked 1000 ml flask fitted with a reflux condenser connected with a $CaCl_2$ tube, a thermometer, a dropping funnel closed by a stopper and a magnetic stirrer, approx. 3% (11 g) of the above mentioned reaction solution was poured. The mixture was stirred intensively by a magnetic stirrer. $3.28 \cdot 10^{-5}$ mole, half of the total amount of $H_2[PtCl_6] \cdot 6H_2O+2-PrOH$, was injected into the reaction solution. After an induction period of about 20 seconds the solution began to boil vigorously. The reaction temperature reached 120 °C. Addition of the reaction mixture was started dropwise and the rest of the catalyst was added to the solution.

The mixture started to be heated to the boiling point and was refluxed at 174 °C. Dropping time: 8 hours. Total refluxing time including dropping: 11 hours. The reaction was carried out in a nitrogen atmosphere. The mixture was distilled at 100 – 103 °C/59 Pa. Yield: 0.86 mole (227.2 g) 65.6%.
Observed $nd^{20°} = 1.4129$. Literature data [11]: 104 °C/60 Pa;
$nd^{20°} = 1.4130$.

2.1.2.2 Preparation of 3-(triethoxy-silyl)-propyl pelargonate, TESPP, (Eq. (4))

A mixture of 1.74 moles of allyl pelargonate and 1.74 moles of $HSi(OC_2H_5)_3$ was prepared. Into the same arrangement described in 2.1.2.1 approx. 10% of the reaction solution (60 g) was poured. The total amount of catalyst was added during intensive stirring to the reaction mixture. After an induction period of about 30 seconds the mixture began to boil, accompanied by foam formation and the reaction temperature attained 130 °C. The solution turned yellow, then brown and remained transparent. The starting period of the reaction, 20 seconds, was not so vigorous as with TESPA. After quieting of the reaction the heating of the solution up to 184 °C was started along with the dropwise dosing of the reaction mixture. The time of dropping was 8 hours, total refluxing time: 10 hours. The reaction was carried out in a nitrogen atmosphere. The mixture was distilled: 146 °C/39 Pa, yielding 1.09 moles (393.9 g), 62%.

2.1.2.3 Preparation of 3-(triethoxy-silyl)-propyl stearate, TESPS, (Eq. (6))

A mixture of 0.82 mole of allyl stearate and 0.82 mole of $HSi(OC_2H_5)_3$ was prepared and heated to 50 °C to keep the mixture above the melting point of allyl stearate. 10% of the reaction mixture was poured into a three-necked flask of the arrangement given in 2.1.2.1 and was heated to 40 °C in order to keep the mixture in the liquid state. The total amount of the catalyst was added. After an induction period of approx. 30 seconds the reaction started and the temperature rose to 120 °C. The solution became light brown. The intensive foam formation stopped after 30 seconds and the dropwise addition of the rest of the reaction mixture was started and the whole solution was brought to 188 °C. Time of dropping: 8 hours, total reaction time: 10 hours. The reaction was carried out in a nitrogen atmosphere. The solution was distilled at 210 – 215 °C/26 Pa giving a yield of 0.46 mole (223.5 g), 56%.

The physical properties of the compounds are summarized in *Table 1a* and *1b*.

Table 1a
Physical properties of the prepared compounds

Compound	Yield % mass	Molar °	Boiling point kg/m^3	Density nd*	
3-(triethoxy-silyl)-propyl acetate	65.6	264	100 – 103/59 Pa	980.0	1.4129
3-(triethoxy-silyl)-propyl pelargonate	62	362	146/39 Pa	943.3	1.4298
3-(triethoxy-silyl)-propyl stearate	56	488	210-215/26 Pa	841.0*	1.4330*

* 40 °C

Table 1b
Elemental analysis of the prepared compounds

Compound	Elemental analysis							
	C%		H%		O%		Si%*	
	calc.	found	calc.	found	calc.	found	calc.	found
3-(triethoxy-silyl)-propyl acetate	50.00	50.30	9.10	9.00	30.30	30.20	10.60	10.50
3-(triethoxy-silyl)-propyl pelargonate	59.70	60.00	10.50	10.30	22.10	22.20	7.70	7.50
3-(triethoxy-silyl)-propyl stearate	66.40	66.70	11 .50	11.56	16.40	16.30	5.70	5.44

* the Si content 'found' was calculated from the found values of C, H and O

2.2. Characterisation of the Hydrosilylated Allyl Esters of Aliphatic Acids

2.2.1 Infrared Spectroscopy

The IR spectra of the investigated compounds were recorded with a Mattson Unicam 3000 FTIR instrument. KBr plates were used for the liquids and KBr pellets for the solids.

At 1740 cm^{-1} all the three spectra show an intense peak assigned to the carboxyl C=O stretching vibration. In the region 2852–2976 cm^{-1}

Table 2
Infrared spectrum of TESPA, TESPP and TESPS

TESPA			TESPP			TESPS		
Wave number [cm^{-1}]	Intensity	Assignment	Wave number [cm^{-1}]	Intensity	Assignment	Wave number [cm^{-1}]	Intensity	Assignment
2976	s	$\nu_{as}CH_3$	2956	s	$\nu_{as}CH_3$	2972	s	$\nu_{as}CH_3$
2927	ms	$\nu_{as}CH_2$	2927	s	$\nu_{as}CH_2$	2922	s	$\nu_{as}CH_2$
2890	ms	ν_sCH_3, CH_2	2872	ms		2852	s	ν_sCH_3, CH_2
1743	s	ν C=O	2857	s	ν_sCH_3, CH_2	1742	s	ν C=O
1486	w	δCH_2	1739	ν s	ν C=O	1467	ms	δCH_2
1443	m	$\delta_{as}C - CH_3$ β_sCH_2	1466	m	δCH_2	1419	w	ν Si–C
1414	w	β_sCH_2 ν Si–C	1441	w	$\delta_{as}C - CH_3$	1391	m	$\delta_sC - CH_3$ Si–O–C
1391	ms	$\delta_sC - CH_3$ Si–O–C	1416	w	β_sCH_2 ν Si–C	1357	w	δ_sCH_3
1366	ms	δ_sCH_3	1391	ms	δ_s, C–CH_3 Si–O–C	1295	w	
1238	s	ν_{as} C–O–C Si-C	1360	w	δ_sCH_3	1245	w	
1198	m	ν_{as} C–O–C Si–O–C	1295	w		1168	s	ν_{as} C–O–C Si–O–C
1167	m	ν_{as} C–O–C Si–O–C	1250	w		1104	s	ν C–O–C Si–O–C
1104	s	ν_s C–O–C Si–O–C	1195	ms	ν_{as} C–O–C Si–O–C	1081	s	ν_s C–O–C Si–O–C
1082	s	ν_s C–O–C Si–O–C	1167	s	ν_{as} C–O–C Si–O–C	959	ms	ν Si–O–C
959	s	ν Si–O–C	1105	s	ν_s C–O–C Si–O–C	892	w	
880	w	Si–C	1081	s	ν_s C–O–C Si–O–C	793	ms	C=O
840	w	δCH_3	959	s	ν Si–O–C	721	w	
790	ms	C=O	886	w	Si–C	643	w	
780	w		843	w				
635	w		794	ms	C=O			
606	w		772	w				

Abbreviations: vs = very strong; s = strong; ms = medium strong; m medium; w = weak;

three intense peaks of CH_3 and CH_2 can be seen. For TESPA the νCH_3 is stronger than $\nu_{as}CH_2$ and ν_sCH_3, CH_2. For both TESPP and TESPS the $\nu_{as}CH_2$ peaks, because of the higher number of CH_2 groups, are significantly stronger than $\nu_{as}CH_3$ and ν_sCH_3, CH_2. In each spectrum the typical band of the double bond of the allyl group at 1650 cm^{-1} has disappeared indicating the addition of H–Si at the double bond.

In comparison with the spectra of the corresponding allyl esters a very strong double peak appears for all the three compounds at 1082–1105 cm^{-1} which can be defined as the stretching vibration mode of Si–O–C and C–O–C.

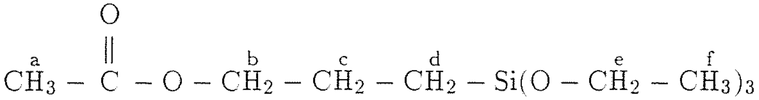
In general it can be stated that all the three spectra – especially those of TESPP and TESPS – have similar shapes with almost the same number of peaks of naturally different widths and intensities and with some differences in the wave numbers indicating that the three compounds belong to the same product group.

2.2.2 Nuclear Magnetic Resonance Spectroscopy ^{1}H-NMR

The measurements were carried out by a Bruker AW 80 instrument at 80 MHz measuring frequency in $CDCl_3$ using TMS as standard. The chemical shifts are given in ppm on a scale, where δTMS = 0 ppm. The following abbrevations were used: s = singlet, d = doublet, t = triplet, qa = quartet, qu = quintet, m = multiplet.

The expected structures of the prepared compounds could be identified on the basis of the ^{1}H-NMR investigations.

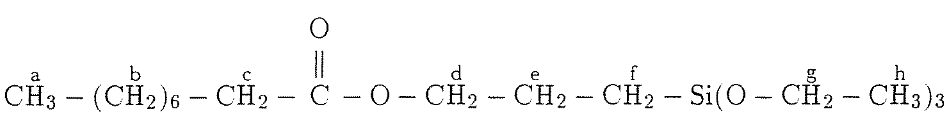
TESPA



$$\overset{a}{CH_3} - \overset{\overset{O}{\|}}{C} - O - \overset{b}{CH_2} - \overset{c}{CH_2} - \overset{d}{CH_2} - Si(O - \overset{e}{CH_2} - \overset{f}{CH_3})_3$$

$\delta_a = 2.03$ ppm (s); $\delta_b = 3.97$ ppm (t); $\delta_c = 1.78$ ppm (qu); $\delta_d = 0.73$ ppm (t); $\delta_e = 3.63$ ppm (qa); $\delta_f = 1.28$ ppm (t)

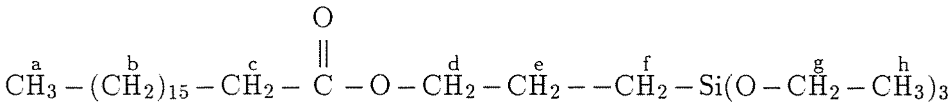
TESPP



$$\overset{a}{CH_3} - (\overset{b}{CH_2})_6 - \overset{c}{CH_2} - \overset{\overset{O}{\|}}{C} - O - \overset{d}{CH_2} - \overset{e}{CH_2} - \overset{f}{CH_2} - Si(O - \overset{g}{CH_2} - \overset{h}{CH_3})_3$$

$\delta_a = 1.25$ ppm (t); $\delta_b = 1.64$ ppm (m); $\delta_c = 2.57$ ppm (t); $\delta_d = 4.19$ ppm (t); $\delta_e = 1.97$ ppm (qu); $\delta_f = 1.12$ ppm (t) $\delta_g = 3.98$ ppm (qa); $\delta_h = 1.59$ ppm (t)

TESPS



$$\overset{a}{CH_3}-\overset{b}{(CH_2)_{15}}-\overset{c}{CH_2}-\overset{\overset{O}{\|}}{C}-O-\overset{d}{CH_2}-\overset{e}{CH_2}--\overset{f}{CH_2}-Si(O-\overset{g}{CH_2}-\overset{h}{CH_3})_3$$

$\delta_a = 0.9$ ppm (t); $\delta_b = 1.27$ ppm (m); $\delta_c = 2.3$ ppm (t); $\delta_d = 4.02$ ppm (t); $\delta_e = 1.6$ ppm (qu); $\delta_f = 0.9$ ppm (t) $\delta_g = 3.84$ ppm (qa); $\delta_h = 1.2$ ppm (t)

For all the three compounds the related δ-values, the form and the intensity of the peaks are in good agreement with the expected structure. In comparison with the spectra of the allyl esters the peaks of the aliphatic part are recognisable in both spectra: TESPP and TESPS have the peaks of a–CH_3, b–CH_2, c–CH_2 in the same position as in the related allyl esters: $\delta_a = 0.9$ ppm; $\delta_b = 1.28$ ppm; $\delta_c = 2.3$ ppm, the hydrosilylation has practically no effect on this region of the NMR spectrum. It is also true for the a–CH_3 of TESPA and the a–CH_3 of allyl acetate, for both the shift is 2.03 ppm. For TESPS and TESPP the differentiation of the h–CH_3 and b–CH_2 is not so obvious, the triplet of h–CH_3 coincides with the huge peak of b–CH_2. The same problem arises for TESPS concerning the identification of a–CH_3 and f–CH_2: $\delta_f = \delta_a = 0.9$ ppm.

3. Conclusions

The synthesis of the triethoxy-silyl derivatives of aliphatic carboxylic acid allyl esters, 3-(triethoxy-silyl)-propyl acetate, 3-(triethoxy-silyl)-propyl pelargonate and 3-(triethoxy-silyl)-propyl stearate was successful and their analytical investigations were carried out. The results obtained for 3-(triethoxy-silyl)-propyl acetate are in good agreement with literature data [11].

The most interesting question was the position of the addition of $HSi(OC_2H_5)$. IR and ^{1}H-NMR spectroscopy results indicated that the C=O, an attackable bond of the allyl esters remained untouched (strong and typical C=O vibration peak in the IR spectra). In all the ^{1}H-NMR spectra the existence of the quintet assigned to the α-CH_2 in the propyl group confirms the β-position of the triethoxy-silyl group. It means that all the three reactions result in β-adducts corresponding to expectations when hexachloro-platinic acid is used as a catalyst.

It is interesting to note that introducing the triethoxy-silyl group in allyl stearate, the melting point decreases from 36.5 °C to room temperature, and vacuum distillation, though at high temperatures (215 °C), is also possible.

The goal of the preparation of these compounds is to use them as coupling agents for $CaCO_3$ and other clay minerals in order to achieve better mechanical properties of the filler-polymer matrix system.

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