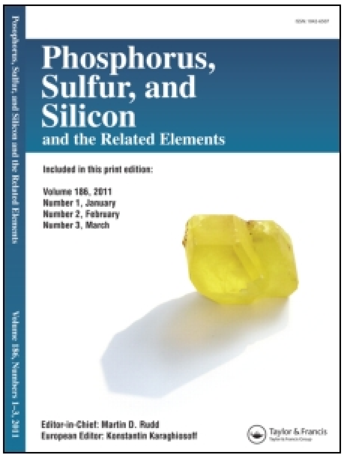

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The Catalytic Isomerization of Terminal Carbon-Carbon Double Bonds in Liquid Crystalline Polyesters at Hydrosilation with 1-(1'-Arylethoxy)-1,1,3,3-Tetramethyl Disiloxanes

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In the present article, we report on the synthesis and investigation of the hydrosilylation of liquid crystalline compounds with terminal carbon–carbon double bonds in aliphatic tails mediated by complexes of rhodium (I) and platinum (II). New liquid crystalline compounds based on terephthaloyl-bis-4-oxybenzoate with terminal carbon-carbon double bonds in aliphatic tails were synthesized. The introduction in aliphatic tails of polar and light polarizible fragments lead to a decrease of mesomorphogenic ability-resulting compounds. The hydrosilylation of liquid crystalline compounds with terminal carbon-carbon double bonds in aliphatic tails with 1-(1′-arylethoxy)-1,1,3,3-tetramethyl disiloxanes mediated by complexes of rhodium (I) and platinum (II) was investigated. The main process in these conditions was the isomerization of olefin fragments.

Keywords Dialkenyl terephthaloyl-bis-4-oxybenzoates; hydrosilylation; isomerization of olefins

INTRODUCTION

The amount of data for synthesized liquid crystalline (LC) compounds containing iloxane fragments are limited, despite the fact that the total number of LC compounds exceeds several tens of thousands.[1] However, these LC compounds have excellent properties, including

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Address correspondence to Vjacheslav V. Zuev, Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi pr.31, Sankt Petersburg 199004, Russian Federation. E-mail: zuev@hq.macro.ru pyro- and piezoelectricity in a ferroelectric LC phase with very high values of pyroelectric and piezoelectric coefficients, and one of the highest values of spontaneous polarization and low switching time.[2–4] Dimethyl siloxane groups are bulky and more flexible and exhibit more irregular conformations compared to their alkyl chain counterparts. This has the effect of reducing the shape anisotropy of the molecules and hence its degree of crystallinity. A reduction of crystallinity to below ambient temperatures is of great interest from an application point of view.

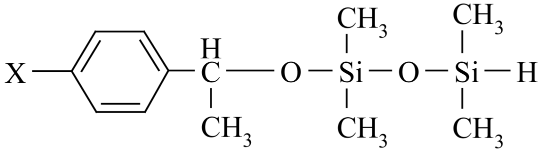
This approach of decreasing crystallinity has already been performed in side chain liquid crystalline polymers.[5] For the synthesis of these polymers, the catalytic hydrosilylation with polymethylhydrosiloxanes of mesogenic compounds are used with a terminal double carbon-carbon bond in the aliphatic tail. The number of used catalysts are limited of a Speier catalyst (1% of H_2PtCl_6 in isopropyl alcohol) and siloxane- platinum (0) complexes (a Karstedt catalyst). The reaction time is typically many days at reaction temperatures 70–90°C and of a multiple excess of a reagent. But even in these conditions, the quantitative conversion of reagents is hardhitting, which leads to defects in the polymer chain and residue Si-H bonds. The presence of Si-H bonds leads to an instability of the polymer properties in the time and formation of three-dimensional networks.[5]

For these reasons, the introduction in LC compounds, the dimethyl siloxane fragments, and a search of new effective catalysts for the hydrosilylation of LC compounds and polymers are a topic of current importance. In the present article, we report on the synthesis and investigation of the hydrosilylation of LC compounds with terminal carbon-carbon double bonds in aliphatic tails mediated by complexes of rhodium (I) and platinum (II).

RESULTS AND DISCUSSION

We have chosen as reagents for hydrosilylation a cheap and available 1,1,3,3-tetramethyl disiloxane and 1-(1′-arylethoxy)-1,1,3,3-tetramethyl disiloxanes **1a–d** (Scheme 1), which have been synthesized by the hydrosilylation of para-substituted acetophenones using several coupling catalysts.[6] The use of chiral compound **1b** allows synthesizing ferroelectric LC compounds.

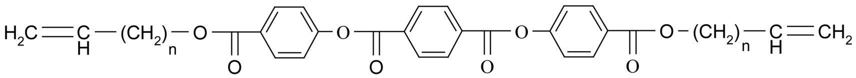
The aliphatic esters of terephthaloyl-bis-4-oxy benzoate with terminal carbon-carbon double bonds **2a–b** (Scheme 2) have been chosen as substrates for hydrosilylation. These compounds have a mesogenic fragment potential, which allow it to form a liquid crystalline state.[1] In addition, they may be synthesized as an attractive method by



1a X=H, **1b** X=OCH$_3$, **1c** X=F, **1d** X=Cl

SCHEME 1

acceptorless high temperature condensation from the readily available terephthaloyl-bis-oxybenzoyl chloride and corresponding alcohol.[7,8]



2a n = 1, **2b** n = 9

SCHEME 2

The LC properties of compounds **2a–b** differ greatly from their saturated analogues thereof presence of double carbon bonds in aliphatic tail. For instance, di-n-propyl terephthaloyl-bis-oxybenzoate have a stable smectic A phase in temperature interval 194–231°C.[8] Moreover, lower fusible compound **2a**($T_m = 139^\circ$C) is not LC. This behavior might be attributed to a presence of double carbon bonds in allyl fragment, which is light polarizible and might interact with phenyl rings of the mesogenic fragment that prevent the formation of a layer structure. This effect supports the active role of an aliphatic tail in the formation of an LC state. The presence long paraffin fragment in the aliphatic tail of **2b** leads to a formation of it a LC state of smectic A type ($T_m = 132^\circ$C, $T_i = 140^\circ$C) (Figure 1). This supports the microscopic observation. Compound **2b** forms in an LC state homeotropic or the focal-conic fan textures (Figure 2). The focal-conic fan texture separates from the isotropic liquid in the form of b$_a$tonnets, which themselves consist of growing focal-conic domains.[9] However, the temperature stability of the mesophase is also lower than on saturated analogous (for decyl derivative 147–165°C[8]).

Ferroelectric LC materials exhibiting r.t. chiral smectic C or chiral smectic A phases and low melting temperatures are of great interest in the electro-optic field. They are the basis of a variety of potential devices ranging from large-area flat-panel displays, ultrafast electro-optic modulators, and spatial optical modulators. They are also considered for novel nonlinear optical applications. Chiral smectic C materials are

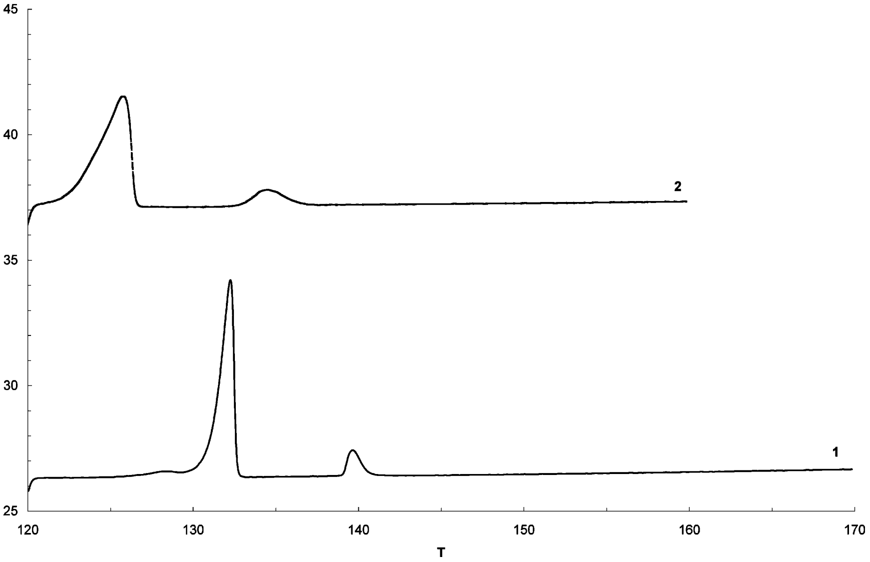
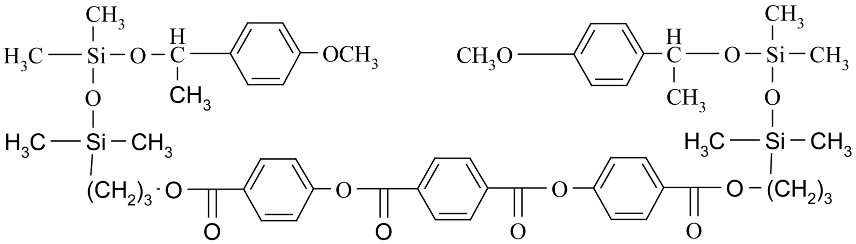


FIGURE 1 The DSC curves of compounds **2b** (1) and **4** (2) at heating rate 2°C/min.

appropriate for an application where bistability is required, whereas chiral smectic A materials are suited for gray-scale application. For these purposes, the hydrosilation of compound **2** with chiral silyl ether **1b** mediated by a Karstedt catalyst was carried out. The interaction of **2a** with **1b** takes place according to the Farmer rule and gives with 90% yield compound **3** (Scheme 3).



3

SCHEME 3

Compound **3** has $T_m = 185°C$ and is not LC. Its specific optical rotation ($[\alpha]_D^{20} = +27.0°$ in chloroform) much increases as compared to that of starting silyl ether **1b** ($[\alpha]_D^{18} = +1.05°$ in ethanol[6]). The same effects

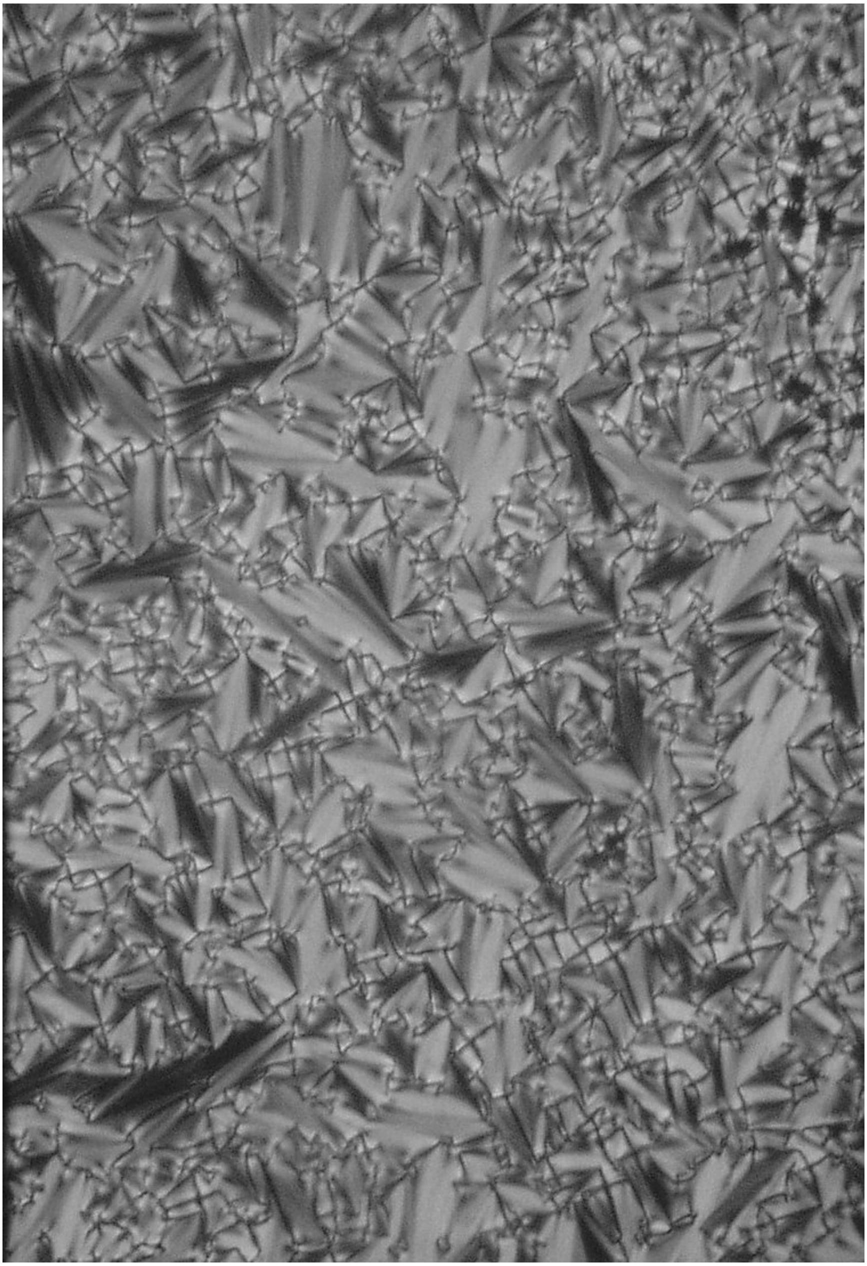
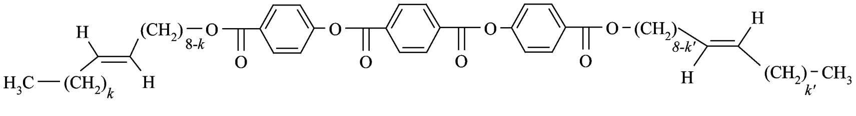


FIGURE 2 The focal-conic fan texture of the smectic A phase of di-10-undecyl terephthaloyl-bis-4-oxybenzoate **2b** at 134°C.

are frequently observed at the synthesis of polymers and LC compounds with elongated hard fragments and are connected with an influence of supramolecular structures.[10]

In contrast to compound **2a**, an interaction of **2b** with **1b** (molar ratio 1:2.5) mediated by a Karstedt catalyst did not lead to a hydrosilylation product. As result of this reaction, the 100% conversion of **2b** yields a mixture of reduction product—diundecyl terephthaloyl-bis-4-oxybenzoate (yield 11.2%)—and a mixture of trans isomers of diundecene terephthaloyl-bis-4-oxybenzoate **4** (Scheme 4) (total yield 88.2%). According NMR data, the ratio of $(CH_2)_{(k+k')}$ groups is 33.2: 36.7:30.1 for *k,k′* = 0, 1, and 2, correspondingly.

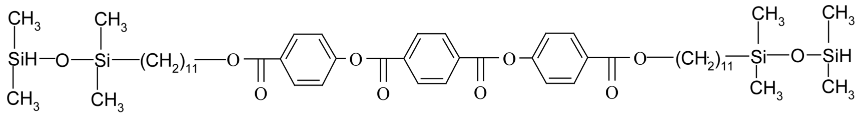


4 *k,k′*=0-2

SCHEME 4

The blank experiment of heating **2b** with a Karstedt catalyst in methylene chloride solution did not give any change of **2b**. Therefore, the silyl ether **1b** plays the main role in the transformation of **2b**. The use of the Wilkinson catalyst $[Rh(Ph_3P)_3Cl]$ instead of the Karstedt catalyst leads to the disappearance of a reduction process at 100% conversion of **2b**, but the main products of the reaction remains a mixture of **4**. According NMR data, the ratio of $(CH_2)_{(k+k')}$ groups is 36.5:38.4:25.1 for k,k′ = 0, 1, and 2, correspondingly. The LC properties of a nonseparated mixture of isomers of **4** practically did not change as compared to **2b**. It has a smectic A phase in the temperature range 126–132°C (Figure 1). The decrease of the melting point is connected with the fact that **4** is of a nonseparated mixture of isomers. The same type of mesophase of compounds **2b** and **4** support the practically equal values of enthalpies of the LC-isotopic melt transition (7.6 J/g, and 7.5 J/g, respectively) and the same focal-conic fan texture of mesophase melts.

We were surprised to find the impossibility of the hydrosilylation of compound **2** with different silyl ethers **1a–d** (the variation of ethers with different X = H, F, and Cl gave the same result). The hydrosilylation of α-alkenes with siloxanes is a well-known process.[11–14] The isomerization accompanies this reaction only as a minor process.[11,14,15] In contrast, the reaction of **2b** with the 6 equivalent of 1,1,3,3-tetramethyl disiloxane mediated by a Karstedt catalyst produces only the hydrosilylation product **5** (Scheme 5) in a quantitative yield.

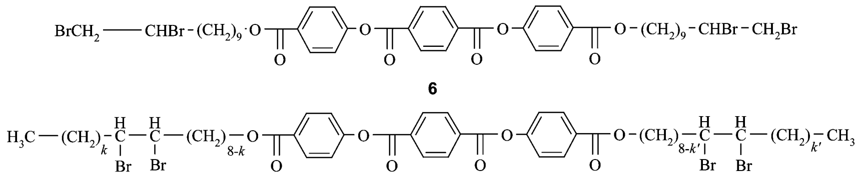


5

SCHEME 5

Compound **5** has a smectic A phase in the temperature range 130–139°C, i.g. practically the same as compounds **2b** and **4**.

To verify the accuracy of the attribution of signals in NMR spectra of compounds **2** and **4**, they were brominated. It affords compounds **6** and **7** (Scheme 6).



6

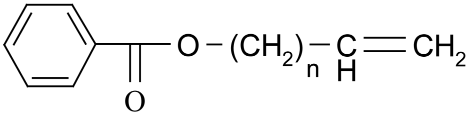
7

SCHEME 6

Compounds **6** and **7** are not LC (T_m is 98°C and 102–104°C correspondingly).

Hence, the introduction of polar or light polarizible groups in an aliphatic tail of a molecule leads to the disappearance their LC properties or to a decrease of the temperature range of a mesophase existence. It is connected with the changing of an anisotropic orientation-dependent interaction of a dispersion kind and disturbance of layer order that is a major factor of the formation of the LC order.[16]

The double-bond isomerization of olefinic hydrocarbons has been mediated by acids, bases, and metal complexes of Pd, Pt, Rh, or Ru.[17,18] There are two possible mechanisms of isomerization for metal complexes. First needs in hydrogen from the outside and be called mechanism of addition-elimination of metal hydride. Second, it has been suggested that the isomerization take place via π-complexes. It does not need the hydrogen from the outside and carries out via a hydrogen 1,3-shift. In our case the isomerization did not take place in the presence of a Karstedt catalyst without silyl ether, which makes preferable the first mechanism of isomerization. For a detailed investigation of this process, we synthesized benzoyl esters **8a–b** (Scheme 7) because it allowed us to investigate the hydrosilylation products also by gas chromatography.

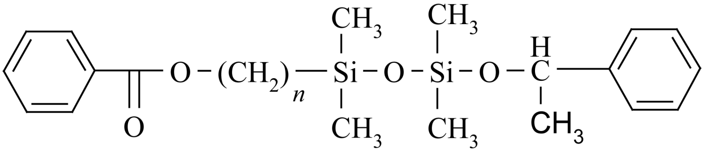


8a n=1, **8b** n=9

SCHEME 7

As a catalyst, we chose traditionally for the hydrosilylation complexes of Pt and Rh.[13] The selection of catalytic complexes was based on their solubility in the reaction mixture because hydrosilylation takes place in homogeneous conditions. We used the Wilkinson catalyst $[Rh(Ph_3P)_3Cl]$ as well as 1-methylcycloocta-1,5-diene (MCOD) complexes $[Rh(MeCOD)Cl]_2$. Also the platinum (II) complexes *cis*-$[Pt(Et_2SO)_2Cl_2]$ and $[Pt(MeCOD)Cl_2]$ were selected.

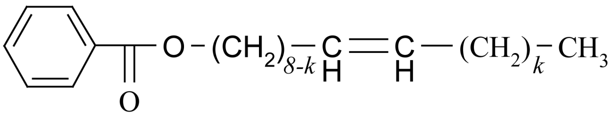
In a reaction of allyl benzoate **8a** with silyl ether **1a** mediated by these catalysts hydrosilylation product **9a** (Scheme 8) 1-[3-(phenyloxycarbonyl)propyl]-3-(1′-phenylethoxy)-1,1,3,3-tetramethyldisiloxane- was obtained in a quantitative yield.



9a n=3, **9b** n=11

SCHEME 8

In contrast to allyl derivatives in a reaction of **1a** mediated by the Wilkinson catalyst in the case of 10-undecyl benzoate, the yield of **9b** (Scheme 8) is 32%, and for $[Rh(MeCOD)Cl]_2$, it is 30%. The main products of these reactions are trans-undecyl benzoates **10** (Scheme 9) with k from 0 to 2 (the same as the case of compound **2b**). For example, the



10 *k*=0-2

SCHEME 9

ration of $(CH_2)_k$ group in a reaction mediated by the Wilkinson catalyst is 36.0:28.8:35.2 for $k = 0$, 1, and 2 correspondingly.

The use of platinum (II) complexes as catalysts leads to higher yields of a hydrosilylation product. In the reaction mediated by [Pt(MeCOD)Cl_2], the yield of **9b** is 55% (a yield of a mixture of **10** is 45%) at a 100% conversion of **8b**. The best result gives cis-[Pt(Et_2SO)$_2Cl_2$] with the yield of **9b** 70% at a full conversion of the starting substrate. If the hydrosilylation is carried out at r.t. (20°C, 48 h), the conversion of substrate decreases, and part of the isomerization increases. In the case of [Rh(MeCOD)Cl]$_2$, the conversion of **8b** is less than 5%, and the products are the mixture of **10**. The use of platinum complex cis-[Pt(Et_2SO)$_2Cl_2$] increases the conversion of **8b** up to 15% with a yield of hydrosilylation product of 8% and an isomerization product of 7%.

The use of reagent 1,1,3,3-tetramethyl disiloxane instead of silyl ethers **1** leads to a quantitative yield of hydrosilylation product **9b** if a reaction occurs at 70°C for 24 h.

Hence, the hydrosilylation of alkenyl esters with 1,1,3,3-tetramethyl disiloxane is suitable for the preparative synthesis of LC compounds, but the use of silyl ethers **1** leads to a complex mixture of many products and will not use a preparative route.

The hydrosilylation of olefins is often accompanied by the isomerization of the double bond. The reaction occurs in the presence of a variety of rhodium compounds.[19] The fact that the isomerization of the double bond accompanies the hydrosilylation was very important for the postulation of the hydrosilylation mechanism by Chalk and Harrod.[20] To make a comparison of isomerization of α-olefins and compounds **2b**, we investigate the behaviour of heptene-1 (70°C, 24 h) in the presence of catalysts [Rh(Ph_3P)$_3$Cl] and cis-[Pt(Et_2SO)$_2Cl_2$]. According NMR data, the part of isomerization for platinum complexes is less than 1%. In the case the use of the Wilkinson catalyst, the part of isomerization increases up to 81% (the ratio of heptene-2 (CH_3, 0.94 ppm):heptene-3 (CH_3, 0.89 ppm) is 52.1:47.9). The interaction at the same condition of heptene-1 with 1-(1′-phenylethoxy)-1,1,3,3-tetramethyl disiloxane **1a** (the molar ratio heptene-1:**1a** is 1:1.2) mediated by *cis*-[Pt(Et_2SO)$_2Cl_2$] leads to a 100% conversion of the substrate and gives 17.3% of isomerization products (heptene-2 and heptene-3 are in about equal proportion) and 82.3% of a hydrosilylation product (1-(1′-phenylethoxy)-3-heptyl-1,1,3,3-tetramethyl disiloxane). In the case of the Wilkinson catalyst, the yield of isomerization products is 71.4% (the ratio of heptene-2:heptene-3 is 49.9:50.1), and part of the hydrosilylation product is 28.6%, i.e., it reproduces a result of the reaction of silyl ethers **1** with benzoate **8b**. If the silyl ether **1a** is changed on 1,1,3,3-tetramethyl disiloxane, yields of the hydrosilylation product are 77% and 23% of a mixture of isomers of heptene.

Hence, the hydrosilylation of ester **2b** takes place similar to the hydrosilylation of α-olefins, but the yield of isomerization products is higher.

The reason for a low reactivity of 1-(1′-arylethoxy)-1,1,3,3-tetramethyl disiloxanes **1a–d** in the hydrosilylation of α-olefines and correspondingly in the activity in isomerization is because of a more strong Si-H bond of this in comparison with 1,1,3,3-tetramethyl disiloxane. According to a calculation with a STO-3G ,basis the partial charge on silicon of Si-H bond is +0.990 for **1a** and only +0.622 for 1,1,3,3-tetramethyl disiloxane. This fact hinders the coordination of silyl ethers **1a–d** on a platinum atom. It leads to a preferable coordination of α-olefin with following isomerization of a double carbon bond. The activity of internal double carbon-carbon bonds in hydrosilylation is low,[11,12] and as result the isomerization dominated.

CONCLUSIONS

In the present article, we report on the synthesis and investigation of the hydrosilylation of LC compounds with terminal carbon-carbon double bonds in aliphatic tails mediated by complexes of rhodium (I) and platinum (II).

New liquid crystalline compounds based on terephthaloyl-bis-4-oxybenzoate with terminal carbon-carbon double bonds in aliphatic tails were synthesized. The introduction in aliphatic tails of polar and light polarizible fragments leads to a decrease of mesomorphogenic ability-resulting compounds.

The hydrosilylation of liquid crystalline compounds with terminal carbon-carbon double bonds in aliphatic tails with 1-(1′-arylethoxy)-1,1,3,3-tetramethyl disiloxanes mediated by complexes of rhodium (I) and platinum (II) was investigated. The main process in these conditions is the isomerization of olefin fragments. The reason for a low reactivity of 1-(1′-arylethoxy)-1,1,3,3-tetramethyl disiloxanes **1a–d** in the hydrosilylation of α-olefines and corresponding activity in the isomerization is a more strong Si-H bond of this incomparison with 1,1,3,3-tetramethyl disiloxane. The use of reagent 1,1,3,3-tetramethyl disiloxane instead of silyl ethers 1 leads to quantitative yield of hydrosilylation products.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX300 spectrometer at 300.13 and 75.468 MHz, respectively. Chemical shifts are reported in ppm relative to $CHCl_3$ (δ 7.26 for ^1H) and $CDCl_3$ (δ 76.9 for ^{13}C).^{1}HNMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), relative intensity, coupling constant (Hz), and interpretation; ^{13}C NMR data are reported as follows: chemical shift in ppm (δ), and interpretation. IR spectra were obtained on a Bruker IFS-88 infrared spectrometer (liquid on KBr disk or in KBr tablets for powder). Specific optical rotations $[\alpha]_D$ were measured with a Perkin Elmer 241A polarimeter for 1% wt solutions in chloroform. A refraction index was obtained on an IFS-22 (USSR) Abbe type refractometer. POM studies have been performed with a Boethius stage (DDR Dresden). Differential scanning calorimetry (DSC) scans were carried out on a Perkin Elmer Pyris 1 instrument. Typically, ca. 4 mg. of a sample were analyzed in each run, while the scan rate was 2°C/min under a nitrogen atmosphere.

The computation was made ab initio method in an orbital basis STO-3G on program HyperChem, version 6.03.

Metal complexes were synthesized following the standard literature methods.[21] 1-(1′-arylethoxy)-1,1,3,3-tetramethyl disiloxanes I a–d were synthesized accordingly.[6]

The hydrosilylation and isomerization were performed in sealed glass tubes at 70°C and at a catalyst concentration of $(1 \div 20) \times 10^{-4}$ mol/L.

Diallyl terephthaloyl-bis-4-oxybenzoate (2a, $C_{28}H_{22}O_8$)

Terephthaloyl-bis-4oxybenzoyl chloride (1 g, 2.25 mmol) and allyl alcohol (3 mL, 44 mmol) was heated in 5 mL of tetradecane at bade temperature 150°C for 30 min. The reaction mixture was poured out in petroleum ether, filtered, and recrystallized from tetradecane. **2a** was obtained as a white crystal with a quantitative yield (1.05 g), m.p. 139°C. IR, cm^{-1}: 1020, 1090, 1120, 1165, 1215, 1280, 1310, 1415, 1468, 1505, 1605, 1720, 1730, 2850, 2920. ^{1}HNMR, δ, ppm (J, Hz): 4.85 d (4H, 4.9), 5.28, 5.34, 5.38, 5.47 (4H, CH_2=), 5.94–6.15 m (2H, CH=), 7.34 d (4H, 8.54), 8.18 d (4H, 8.54), 8.35 s (4H). Found, %: C, 68.72; H, 4.42. $C_{28}H_{22}O_8$. calcd. %: C,69.13; H, 4.560

Di-10-undecyl terephthaloyl-bis-4-oxybenzoate (2b, $C_{44}H_{54}O_8$)

The same procedure was used for preparation. White solid, m.p. 134°C. IR, cm^{-1}: 1020, 1075, 1085, 1120, 1160, 1215, 1285, 1310, 1410, 1465, 1505, 1605, 1710, 1730, 2850, 2920, 2950. ^{1}H NMR, δ, ppm (J, Hz):

1.31 (shoulder 1.38) broad s (24H), 1.71–1.82 m (4H), 1.99–2.09 m (4H), 4.34 t (4H, 7.5), 4.91–5.03 m (4H, CH_2=), 5.71–5.91 m (2H,CH=), 7.34 d (4H, 8.54), 8.16 d (4H, 8.54), 8.35 c (4H). ^{13}C NMR, δ, ppm: 65.22 (OCH_2, α), 29.33 (β), 25.89 (γ), 28.59 (δ), 28.97 (ε), 29.27 (ζ), 29.12 (η), 28.79 (θ), 33.66 (ι), 139.06 (CH=), 114.0 (CH_2=), 163.56 (CO, terephthaloyl), 133.57 (ipso), 130.28 (ortho), 165.67 (CO, benzoyl), 128.40 (ipso), 131.14 (ortho), 121.45 (meta), 154.06 (para). Found, %: C, 74.72; H, 7.54. $C_{44}H_{54}O_8$. calcd %: C, 74.34; H, 7.66.

(+)-di[4-(3-{1-(1-[para-methoxyphenyl]ethoxy)-1,1, 3, 3-tetramethyl disiloxane} propyl) oxybenzoyl]terephthalate (3)

160 mg (0.3 mmol) of **2a** and 400 mg (0.8 mmol) of **1b** were heated in a sealed tube with a solution of a Karstedt catalyst in methylene chloride ($C_{cat}1.5\times 10^{-3}$ mol/L) at 70°C for 21 h. The reaction mixture was passed througha thin layer of silica on a Shot funnel; silica was washed with a small amount of methylene chloride, and unified filtrate was poured out in petroleum ether. The residue was filtered up and once again precipitated from methylene chloride to petroleum ether. Yield 280 mg (90%) of **3** as white crystals, m.p. 185°C. $[\alpha]_D^{20} = +27.0^\circ$ (δ0.2C, HCl_3). IR, cm^{-1}: 703, 805, 960, 1020, 1060, 1103, 1275, 1410, 1450, 1600, 1715, 1730, 2850, 2950, 3025, 3060. ^1H NMR, δ, ppm (J, Hz): 0.08, 0.12, 0.13 (24H, Si-CH_3), 0.50–0.57 m (4H, Si-CH_2),1.74–1.88 m (4H, CH_2), 3.79 s (6H, OCH_3), 4.31 t (4H, 6.9), 7.34 d (4H, 8.54), 8.16 d (4H, 8.54), 8.35 s (4H), 6.86 d (4H, 8.54), 7.38 d (4H, 8.54).

A mixture of Di-undecyl terephthaloyl-bis-4-oxybenzoate(4)

The same procedure was used for its preparation with a 95% yield as a white solid, m.p. 134°C. IR, cm^{-1}: 1020, 1075, 1085, 1120, 1160, 1215, 1285, 1310, 1410, 1465, 1505, 1605, 1710, 1730, 2850, 2920, 2950. ^1H NMR, δ, ppm (J, Hz): 1.30–1.45 m (24H), 1.75–1.84 m (4H), 1.96–2.08 m (6H), 1.60–1.67 m (2H), 4.34 t (4H, 7.5), 5.35–5.50 t (4H, CH=), 7.34 d (4H, 8.54), 8.16 d (4H, 8.54), 8.35 s (4H); k = 0 0.98 t (CH_3), k = 1 0.91 t (CH_3), k = 2 0.90 t (CH_3). ^{13}C NMR, δ, ppm: 65.19 (OCH_2, α), 163.56 (CO, terephthaloyl), 133.57 (ipso), 130.28 (ortho), 165.67 (CO, benzoyl), 128.40 (ipso), 131.14 (ortho), 121.45 (meta), 154.06 (para); k = 0 17.77 (CH_3), 124.45 (=CH CH_3), 131.44 (=CH), 34.54 (θ), 28.8–29.4 ($\beta - \eta$); k = 1 13.86 (CH_3), 131.85 (=$CHCH_2CH_3$), 129.08 (=CH); k = 2 13.96 (CH_3), 133.64 (=$CH(CH_2)_2CH_3$), 129.66 (=CH), 32.43 (=$CH\underline{C}H_2$), 32.36 ($\underline{C}H_2CH_3$).

Di{4-(11-[1,1,3,3-Tetramethyldisiloxane]undecyl)-oxybenzoate}terephthalate(5, $C_{52}H_{68}O_{10}Si_4$)

210 mg (0.3 mmol) of **2b** and 0.4 mL (2.4 mmol) of 1,1,3,3-tetramethyl disiloxane were heated in a sealed tube with a solution of a Karstedt catalyst in methylene chloride (C_{cat} 1.42×10^{-3} mol/L) at 70°C for 21 h. The reaction mixture was passed through a thin layer of silica on a Shot funnel; silica was washed with small amount of methylene chloride; a unified filtrate was poured out in petroleum ether. The residue was filtered up and once again precipitated from methylene chloride to petroleum ether. Yield 260 mg (90%) of **5** as white crystals, m.p. 130°C. IR, cm^{-1}: 703, 805, 960, 1020, 1060, 1103, 1275, 1410, 1450, 1600, 1715, 1730, 2850, 2950, 3025, 3060. ^1H NMR, δ, ppm (J, Hz): 0.08, 0.12, 0.13 (24H, Si-CH_3), 0.50–0.57 m (4H, Si-CH_2), 1.33 broad s (24H), 1.63 broad s (4H), 1.79–1.84 m (4H), 4.31 t (4H, 6.9), 7.34 d (4H, 8.54), 8.16 d (4H, 8.54), 8.35 s (4Õ). Found%: C, 64.32; H, 6.83; Si, 11.32. $C_{52}H_{68}O_{10}Si_4$. calcd. %: C, 64.69; H, 7.10; Si, 11.64.

Di(10,11-Dibromineundecyl)-terephthaloyl-bis-4-oxybenzoate (6, $C_{44}H_{54}O_8Br_2$)

To a solution of 0.5 g (0.75 mmol) of **2b** in 3 mL of chloroform was added 1 mL of bromine. After 30 min, the solution was poured in methanol and filtered, and a residue was recipitated from chloroform to methanol. Yield 0.6 g of **6** (quantitative), m.p. 98°C IR, cm^{-1}: 715, 880, 1020, 1072, 1095, 1112, 1162, 1275, 1310, 1455, 1465, 1502, 1605, 1720, 1730, 2850, 2920.^1H NMR, δ, ppm (J, Hz): 1.33 broad s (24H), 1.63 broad s (4H), 1.79–1.84 m (4H), 4.34 t (4H, 7.5), 4.10–4.20 m (2H, CHBr), trans t 3.62 (9.77), cis-dd 3.82, 3.87 (9.77, 4.26) (4H, CH_2Br), 7.34 d (4H, 8.54), 8.16 d (4H, 8.54), 8.35 s (4H). Found %: C, 60.72; H, 6.53; Br, 18.20. $C_{44}H_{54}O_8Br_2$. calcd. %: C, 60.69; H, 6.25; Br, 18.35.

A mixture of Di(dibromineundecyl)-terephthaloyl-bis-4-oxybenzoate (7)

The same procedure was used for its preparation with a 95% yield. M.p. 102–104°C. IR, cm^{-1}: 715, 880, 1020, 1072, 1095, 1112, 1162, 1275, 1310, 1455, 1465, 1502, 1605, 1720, 1730, 2850, 2920. ^1H NMR, δ, ppm (J, Hz): 0.95 (6H), 1.33 broad s (24H), 1.63 broad s (4H), 1.79–1.84 m (4H), 4.34 t (4H, 7.5), 4.10–4.20 m (4H, CHBr), 7.34 d (4H, 8.54), 8.16 d (4H, 8.54), 8.35 s (4H).

Allyl- and 10-undecylbenzoates(**8**) was synthesized by a high-temperature acceptorless condensation from corresponding alcohol and benzoyl chloride. **8a**. B.p. 96°C (5 mm of Hg), $n_D^{20} = 1.5180$ {lit.: b.p. 106 (12 mm of Hg), $n_D^{20} = 1.5180$.[22] **8b** B.p. 162 (2 mm of Hg $n_D^{20} = 1.4967$. IR, cm^{-1}: 1020, 1075, 1085, 1120, 1160, 1215, 1285, 1310, 1410, 1465, 1505, 1605, 1730, 2850, 2920, 2950. ^{1}H NMR, δ, ppm (J, Hz): 1.31 broad s (12H), 1.78 m (2H), 2.06 q (2H, 6.75), 4.34 t (2H, 6.75), 4.93–5.04 m (2H, CH_2=), 5.76–5.90 m (1H, CH=), 7.44 t (2H, 6.75, meta), 7.56_T (1H, 7.5, para), 8.07 ‰ (1H, 6.75, ortho). ^{13}C NMR, δ, ppm: 64.88 (OCH_2, α), 29.27 (β), 25.85 (γ), 28.72 (δ), 28.91 (ε), 29.21 (ζ), 29.07 (η), 28.54 (θ), 33.61 (ι), 138.91 (CH=), 113.94 (CH_2=), 166.41 (CO), 130.36 (ipso), 129.32 (ortho), 128.09 (meta), 132.54 (para).

1-[3-(Phenyloxycarbonyl)propyl]-3-(1′-phenylethoxy)-1,1,3,3-tetramethyl disiloxane (9a, $C_{22}H_{32}O_4Si_2$)

375 mg (2.3 mmol) of allyl benzoate and 540 mg (2.7 mmol) of **1a** (a molar ratio 1:1.2) were heated in a sealed tube with a solution of a Karstedt catalyst in methylene chloride (C_{cat} 1.42×10^{-3} mol/L) at 70°C for 20 h. The reaction mixture was distillated in vacuum. Yield 560 mg (85%) of **9a** as transparent liquid. B.p. 134°C (2 mm of Hg), $n_D^{20} = 1.4790$. IR, cm^{-1}: 703, 805, 960, 1020, 1060, 1103, 1275, 1410, 1450, 1600, 1730, 2850, 2950, 3025, 3060. ^{1}H NMR, δ, ppm (J, Hz): 0.03, 0.12, 0.13 (12 H, Si-CH_3), 0.4 s (2H, Si-CH_2), 1.56 d (CH_3, 3H, 6.9); 1.78–1.86 m (2H), 4.28 t (2H, 6.9), 7.55 t (1H, 6.75), 7.44 t (2H, 6.75), 8.07 d (2H, 6.75), 5.09 q (CH, 1H, 6.9); 7.33–7.46 m (ortho and para CH, 4H); 7.25–7.31 m (para CH, 1H). Found %: C, 63.72; H, 7.89; Si, 13.68. $C_{22}H_{32}O_4Si_{,2}$. calcd. %: C, 63.42; H, 7.74; Si, 13.48.

1-[11-(Phenyloxycarbonyl)propyl]-3-(1′-phenylethoxy)-1,1,3,3-tetramethyl disiloxane (9b, $C_{32}H_{48}O_4Si_2$)

The same procedure was used for it preparation with a 15% yield as transparent liquid. B.p. 164°C (2 mm of Hg), $n_D^{20} = 1.4771$. IR, cm^{-1}: 703, 805, 960, 1020, 1060, 1103, 1275, 1410, 1450, 1600, 1730, 2850, 2950, 3025, 3060. ^{1}H NMR, δ, ppm (J, Hz): 0.03, 0.12, 0.13 (12 H, Si-CH_3), 0.57 c (2H, Si-CH_2), 1.34 c (16H), 1.49 d (CH_3, 3H, 6.9); 1.79–1.86 m (2H), 4.34 t (2H, 6.9), 7.57 t (1H, 6.75), 7.46 t (2H, 6.75), 8.08 d (2H, 7.5), 5.08 q (CH, 1H, 6.9); 7.30–7.36 m (ortho and para CH, 4H); 7.22–7.31 m(para CH, 1H). ^{13}C NMR, δ, ppm: 64.87 (OCH_2, α), 29.44 (β), 25.86 (γ), 28.56 (δ), 29.36 (ε), 29.27 (ζ), 29.12 (η), 29.51 (θ), 33.28 (ι), 23.06 (κ), 18.08 (λ), 0.02, 088, 0.99 ($SiCH_3$), 26.58 (CH_3), 69.91 (CH), 166.35 (CO), 130.38 (ipso), 129.32 (ortho), 128.08 (meta), 132.52 (para), (benzyl) 146.08 (ipso), 125.12 (ortho), 127.89 (meta), 126.57 (para).

Found %: C, 69.32; H, 8.80; Si, 10.54. $C_{32}H_{48}O_4Si_2$. calcd. %: C, 69.51; H, 8.75; Si, 10.16.

A Mixture of Undecyl Benzoates (10)

B.p. 148–154°C (2 mm of Hg). IR, cm^{-1}: 1020, 1075, 1085, 1120, 1160, 1215, 1285, 1310, 1410, 1465, 1505, 1605, 1730, 2850, 2920, 2950. ^1H NMR, δ, ppm (J, Hz): 1.30–1.45 m (24H), 1.75–1.84 m (4H), 1.96–2.08 m (6H), 1.60–1.67 m (2H), 4.34 t (4H, 7.5), 5.35–5.50 m (4H, CH=), 7.34 d (4H, 8.54), 8.16 d (4H, 8.54), 8.35 s (4H); k = 0 0.98 t CH_3), k = 1 0.91 t (CH_3), k = 2 0.90 t (CH_3). ^{13}C NMR, δ, ppm: 64.87 (OCH_2, α), 166.35 (CO), 130.38 (ipso), 129.32 (ortho), 128.08 (meta), 132.52 (para); k = 0 17.77 (CH_3), 124.45 (=$CHCH_3$), 131.44 (=CH), 34.54 (θ), 28.8–29.4 ($\beta - \eta$); k = 1 13.86 (CH_3), 131.85 (=$CHCH_2CH_3$), 129.08 (=CH); k = 2 13.96 (CH_3), 133.64 (=$CH(CH_2)_2CH_3$), 129.66 (=CH), 32.43 (=$CH\underline{C}H_2$), 32.36 ($\underline{C}H_2CH_3$).

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