L. L. SHCHUKOVSKAYA, R. I. PALCHIK,

Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV

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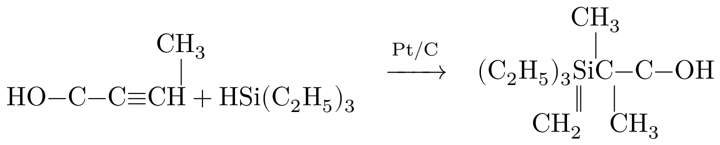
Abstract

Full Text

L. L. SHCHUKOVSKAYA, R. I. PALCHIK,
Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV

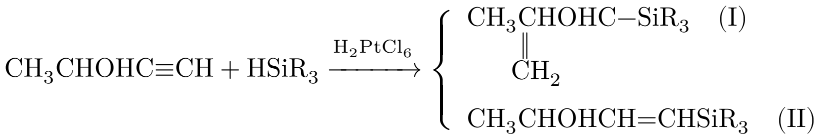
THE ORDER OF ADDITION OF TRIALKYLSILANES TO UNSATURATED ALCOHOLS

Earlier ([1,2]) we carried out the addition of triethylsilane to dimethylethynylcarbinol and methyltrifluoromethylethynylcarbinol in the presence of Pt/C in an autoclave and, on the basis of IR spectra, established that the order of addition does not contradict the scheme:



$$HO-C-C\equiv\overset{\overset{CH_3}{|}}{CH} + HSi(C_2H_5)_3 \xrightarrow{Pt/C} (C_2H_5)_3Si\underset{\underset{CH_2}{\|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{C}-OH$$

In the present work it was established that trialkylsilanes add to the unsaturated alcohols investigated in two directions*:



$$CH_3CHOHC\equiv CH + HSiR_3 \xrightarrow{H_2PtCl_6} \begin{cases} CH_3CHOH\underset{\underset{CH_2}{\|}}{C}-SiR_3 \quad (I) \\ CH_3CHOHCH=CHSiR_3 \quad (II) \end{cases}$$

The formation of two isomeric compounds corresponding to different orders of addition of silicoformic hydride to chloropropyne was recently demonstrated by Mironov ([3]). Figure 1 presents the IR spectra of two pairs of isomeric alcohols corresponding to the I $(2, 4)$ and II $(1, 3)$ directions of addition**.

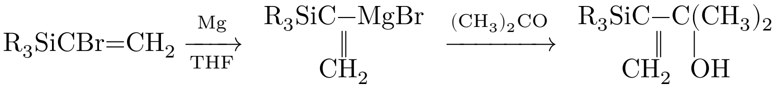
In each pair both isomers are identified by the bands of the stretching vibrations of CH in the groups $C{=}CH_2$ or $CH{=}CH$. In the latter case the $CH{=}CH$ band near 3000 cm^{-1} appears on the slope of the bands of the CH_3 and C_2H_5 groups. The frequencies of the bands of "associated" hydroxyls (higher in tertiary alcohols than in secondary ones) are shifted to longer wavelengths in the isomers containing hydroxyl in the γ-position to silicon to a greater extent than in the isomers with OH in the β-position:

	1	2	3	4
νOH_{acc}	3325	3360	3370	3430

	1	2	3	4
νCH(C=CH_2)	–	3059	(3061)	3061
νCH(CH=CH)	3005sh	–	3011sh	–

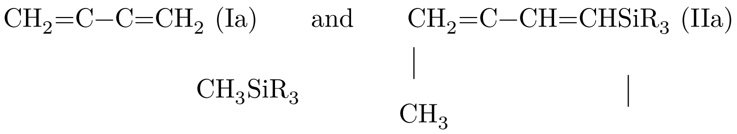
The position of the C=C-vibrations in the spectra of the isomers changes from 1620-1630 cm^{-1} for the CH=CH groups to 1600 cm^{-1} in the C=CH_2 groups.

To prove the structure of the adducts obtained in direction I, a counter synthesis of the corresponding alcohol was carried out according to the scheme:



$$R_3SiCBr{=}CH_2 \xrightarrow[THF]{Mg} \underset{\underset{CH_2}{\|}}{R_3SiC}{-}MgBr \xrightarrow{(CH_3)_2CO} \underset{\underset{CH_2}{\|}}{R_3SiC}{-}\underset{\underset{OH}{|}}{C}(CH_3)_2$$

The IR spectra and properties of both alcohols coincided. The tertiary alcohols obtained the alcohols were dehydrated over $KHSO_4$ with formation of



$$CH_2{=}C{-}C{=}CH_2\ (Ia) \quad \text{and} \quad CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}CH{=}CHSiR_3\ (IIa)$$

$$CH_3SiR_3$$

It should be noted that both β-alcohols obtained did not undergo any noticeable β-decomposition under the dehydration conditions.

Experimental Part

Addition of triethylsilane to methylethynylcarbinol. Into a flask equipped with a reflux condenser, a thermometer, and a dropping funnel was placed a small portion of a mixture of 39 g of methylethynylcarbinol* and 64 g of triethylsilane and 0.2 ml of 0.1 N H_2PtCl_6 solution. When the mixture was boiled, the temperature in the flask gradually rose to 144°. After two fractionations on a column, two isomeric alcohols were isolated.

I. B.p. 76° (2 mm); n_D^{20} 1.4640, d_4^{20} 0.8804; MR_D found 58.41, calculated 59.13.

Found, %:	C 64.79;	H 11.92;	Si 14.81
$C_{10}H_{22}SiO$. Calculated, %:	C 64.44;	H 11.89;	Si 15.07

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* The use of Pt/C as a catalyst also leads to the formation of two isomers.

** For interpretation of the IR spectra the authors express their deep gratitude to A. N. Lazarev.

IR spectrum (ν in cm^{-1})**: 1720 (?), 1688 sh, (1630), 1608, 1468, 1424, 1385, 1374, 1335, 1289, 1245, 1223, 1203, 1189, 1136, 1096, 1074, 1035, 1022 sh, ~1015, 997, 979, 970 sh, 941, 923, 865, 857, 843, 804, 788, ~730, 685.

II. B.p. 86° (3 mm); n_D^{20} 1.4580, d_4^{20} 0.8654; MR_D found 58.76, calculated 59.13

IR spectrum (ν in cm^{-1}): 1715 sl, 1628, 1468, 1424, 1385 sh, 1375, 1334, 1312, 1243, 1218, 1134, 1066, 1035 sh, 1021, 996, 980, 970 sh, 945, 870, 840, 804, 788, ~728, 686.

Addition of methyldiethylsilane to dimethylethynylcarbinol. Two isomers were isolated by fractionation:

I. B.p. 73.5° (5.5 mm); n_D^{20} 1.4590, d_4^{20} 0.8711; MR_D found 58.49, calculated 59.13.

IR spectrum (ν in cm^{-1}): 1715 sl, (1623), 1600 sh, 1467, 1424, 1410, 1382, 1368, 1320, 1257, 1239, 1190 sh, 1166 sh, (1150), 1125, 1020, 1012, (997), 962, 932, 909, 891, 860 sl, 830 sh, 807, 746.

Incomplete separation of the isomers is illustrated by the presence of a C=C band at 1623 cm^{-1} (Figs. 1, 4), not observed in the spectrum of the product of counter synthesis (Fig. 2). The molecular constants were determined for purer isomers subjected to repeated separation.

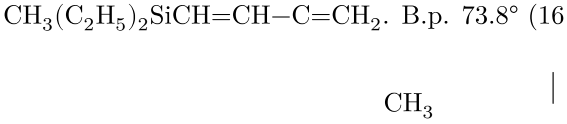
II. B.p. 83.5° (5.5 mm); n_D^{20} 1.4530, d_4^{20} 0.8534; MR_D found 59.05, calculated 59.13.

IR spectrum (ν in cm^{-1}): 1715 sl, 1622, 1468, 1422, (1408), 1379, 1366, 1316, 1256, 1238, 1223, ~1200 sh, 1152, 1139, ~1015, 996, 968, 952, (930 sh), 913, 885 sl, 830, 810, 745, 736.

Literature data (5): b.p. 77° (6.5 mm); n_D^{20} 1.4512, d_4^{20} 0.8568. Dehydration of the alcohols over $KHSO_4$ led to formation of silicon hydrocarbons:

Ia. $CH_3(C_2H_5)_2SiC(=CH_2)-CH=CH_2$. B.p. 70-71° (17 mm); n_D^{20} 1.4617, d_4^{20} 0.8105; MR_D found 57.07, calculated 57.12.

Found, %:	C 71.92;	H 12.19;	Si 15.91
$C_{10}H_{20}Si$. Calculated, %:	C 71.34;	H 11.99;	Si 16.88

IIa. 

$CH_3(C_2H_5)_2SiCH=CH-\underset{CH_3}{\underset{|}{C}}=CH_2$. B.p. 73.8° (16 mm),

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* Methylethynylcarbinol was prepared by the method of Jones (4). The yield reached 71% of theory.

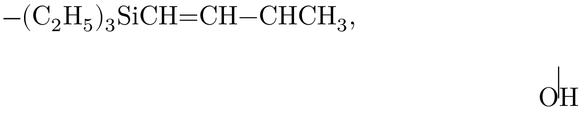
** In parentheses are bands associated with a small impurity of the other isomer; sh—shoulder on the slope of a stronger band.

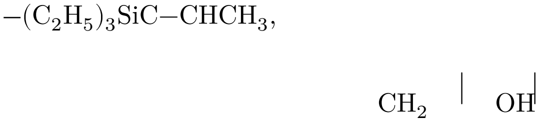
Fig. 1. IR spectra of isomers of secondary and tertiary alcohols containing the hydrosil group in β- and δ-positions with respect to silicon (liquid, layer 0.01 mm).

Figure 1: Fig. 1. IR spectra of isomers of secondary and tertiary alcohols containing the hydrosil group in β- and δ-positions with respect to silicon (liquid, layer 0.01 mm).

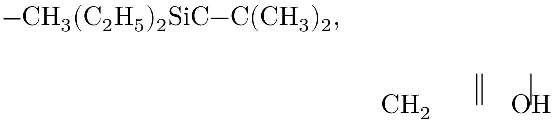
n_D^{20} 1.4680, d_4^{20} 0.8000; MR_D found 58.49, calculated 57.12.

Fig. 1. IR spectra of isomers of secondary and tertiary alcohols containing the hydrosil group in β- and δ-positions with respect to silicon (liquid, layer 0.01 mm):

1 –
$(C_2H_5)_3SiCH{=}CH{-}\underset{\underset{OH}{|}}{CH}CH_3$,

2 –
$(C_2H_5)_3Si\underset{\underset{CH_2}{|}}{C}{-}\underset{\underset{OH}{|}}{CH}CH_3$,

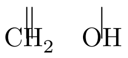
3 –$CH_3(C_2H_5)_2SiCH{=}CH{-}C(CH_3)_2$,

4 –
$CH_3(C_2H_5)_2Si\underset{\underset{CH_2}{\|}}{C}{-}\underset{\underset{OH}{|}}{C}(CH_3)_2$,

Synthesis of α-bromovinylmethyldiethylsilane $CH_3(C_2H_5)_2SiCBr{=}CH_2$. To C_2H_5MgBr, prepared from 26 g Mg and 120 g C_2H_5Br, 110 g of α-bromovinylmethyldichlorosilane was added. 62 g of α-bromovinylmethyldiethylsilane was isolated; b.p. 70° (22 mm); n_D^{20} 1.4690, d_4^{20} 1.1164; MR_D found 51.68, calculated 51.37.

Found, %: Br 38.04. Calculated, %: Br 38.56

Synthesis of β-(methyldiethylsilyl)-dimethylvinylcarbinol $CH_3(C_2H_5)_2SiC{-}C(CH_3)_2$

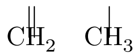

$CH_3(C_2H_5)_2Si\underset{\underset{CH_2}{\|}}{C}{-}\underset{\underset{OH}{|}}{C}(CH_3)_2$

From 7 g of magnesium and 60 g of α-bromovinylmethyldiethylsilane in 200 ml of tetrahydrofuran (THF), a Grignard reagent was prepared, to which 18 g of

Fig. 2. IR spectrum of $CH_3(C_2H_5)_2SiC—C(OH_3)_2$, obtained by counter synthesis (20% solution, layer 0.03 mm). Note the position and relative intensity of the C = C band at 1600 cm^{-1} in comparison with curve 4 in Fig. 1.

Figure 2: Fig. 2. IR spectrum of $CH_3(C_2H_5)_2SiC—C(OH_3)_2$, obtained by counter synthesis (20% solution, layer 0.03 mm). Note the position and relative intensity of the C = C band at 1600 cm^{-1} in comparison with curve 4 in Fig. 1.

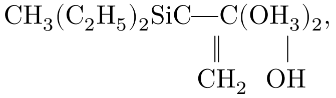
acetone was added. 17 g (yield 31%) of the alcohol was isolated, b.p. 75° (6 mm); n_D^{20} 1.4600, d_4^{20} 0.8737; MR_D found 58.43, calculated 59.13. Dehydration of the alcohol over $KHSO_4$ led to the formation of $CH_3(C_2H_5)_2SiC{-}C{=}CH_2$,


$$\begin{array}{cc} \| & | \\ CH_2 & CH_3 \end{array}$$

b.p. 69-69.5° (17 mm); n_D^{20} 1.4609, d_4^{20} 0.8124; MR_D found 56.85; calculated 57.12.

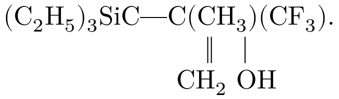
Addition of triethylsilane to methyltrifluoromethylethynylcarbinol. To 7 g of the carbinol, in the presence of H_2PtCl_6, 6 g of triethylsilane was added. The temperature in the flask was maintained at not above 125°. After two fractionations, two isomers were isolated:

Fig. 2. IR spectrum of


$$CH_3(C_2H_5)_2Si\underset{\underset{CH_2}{\|}}{C}—\underset{\underset{OH}{|}}{C}(OH_3)_2,$$

obtained by counter synthesis (20% solution, layer 0.03 mm). Note the position and relative intensity of the C = C band at 1600 cm^{-1} in comparison with curve 4 in Fig. 1.

I.


$$(C_2H_5)_3Si\underset{\underset{CH_2}{\|}}{C}—\underset{\underset{OH}{|}}{C}(CH_3)(CF_3).$$

b.p. 76° (4.5 mm); n_D^{20} 1.4281, d_4^{20} 1.0381; MR_D found 63.04, calculated 63.07.

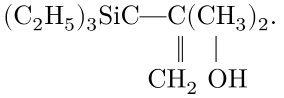
II. $(C_2H_5)_3SiCH = CH—C(CH_3)(CF_3)$.


$$\begin{array}{c} | \\ OH \end{array}$$

b.p. 76.5° (4 mm); n_D^{20} 1.4275, d_4^{20} 1.0327; MR_D found 63.30, calculated 63.07.

Addition of triethylsilane to dimethylethynylcarbinol. To 17 g of the carbinol, under the usual conditions, 24 g of triethylsilane was added. Fractionation on a column yielded:

I.

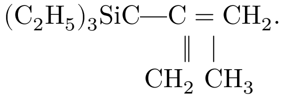


$$(C_2H_5)_3Si\underset{\underset{CH_2}{\|}}{C}—\underset{\underset{OH}{|}}{C}(CH_3)_2.$$

b.p. 87-87.5° (5.5 mm); n_D^{20} 1.4612, d_4^{20} 0.8710; MR_D found 63.15, calculated 63.77.

II. $(C_2H_5)_3SiCH = CH—C(OH)(CH_3)_2$. b.p. 94-94.5° (6.5 mm), n_D^{20} 1.4572, d_4^{20} 0.8710; MR_D found 63.56, calculated 63.77. Dehydration of the alcohols by distillation over $KHSO_4$ led to the formation of silicon hydrocarbons:

Ia.



$$(C_2H_5)_3Si\underset{\underset{CH_2}{\|}}{C}—\underset{\underset{CH_3}{|}}{C} = CH_2.$$

b.p. 93-94° (19 mm); n_D^{20} 1.4682, d_4^{20} 0.8232; MR_D found 61.61, calculated 61.77.

IIa. $(C_2H_5)_3SiCH = CH—C(CH_3) = CH_2$. b.p. 86.5-87° (13 mm); n_D^{20} 1.4730, d_4^{20} 0.8128; MR_D found 62.93, calculated 61.77.

Institute of Silicate Chemistry named after I. V. Grebenshchikov
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