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HYDROSILYLATION OF OLEFINS IN THE PRESENCE OF METAL CARBONYLS

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Summary

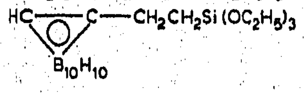
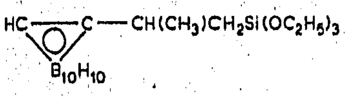
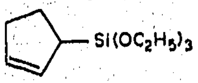
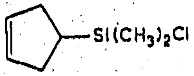
Hydrosilylation of cardinal types of olefins, R'—$CH=CH_2$ ($R' = C_3H_7$—$C_{10}H_{21}$, C_6H_5, $Si(CH_3)_3$, $CH_2N(CH_3)_2$, $CH_2N[Si(OC_2H_5)_3]_2$) and cyclopentadiene with silanes, $HSiR''_nX_{3-n}$ ($n = 1$ or 2, $R'' = CH_3$ or C_2H_5, X = Cl; $n = 0$, X = Cl, OC_2H_5) in the presence of the catalytic metal carbonyls $Co_2(CO)_8$ and $Rh_4(CO)_{12}$, is described Alkylchloro(ethoxy)silanes, $R'CH_2CH_2SiR''_nX_{3-n}$ and cyclopentenylchloro(ethoxy)alkylsilanes are obtained in quantitative yields after reaction times of 30 min to several hours depending on the nature of the metal carbonyl, olefin structure, and reaction temperature. Hydrosilylation of vinyl- and isopropenyl-*o*-carboranes occurs only at 20—30°C over 2—3 days, yields of the corresponding silanes being 20—35%. On interaction of triethoxysilane and allylamine, silylation of the nitrogen atom occurs in the first place, and only after this does hydrosilylation of the double bond occur.

Introduction

It has been shown by some authors [1—3] that dicobaltoctacarbonyl is an effective catalyst in α-olefins hydrosilylation. Our study of the process led us to the conclusion that only carbonyls of rhodium, $Rh_4(CO)_{12}$,iridium, $Ir_4(CO)_{12}$, and cobalt, $Co_2(CO)_8$, catalyze hydrosilylation of α-olefins [4] and vinyltrimethylsilane [5], whereas most metal carbonyls, $Me(CO)_6$ (M = Cr, Mo, W), $Fe(CO)_5$, $Fe_2(CO)_9$, $M_3(CO)_{12}$ (M = Fe, Ru, Os), $M_2(CO)_{10}$ (M = Mn, Re) and their derivatives, $C_6H_6M(CO)_3$ (M = Cr, Mo), $[C_5H_5Fe(CO)_2]_2$ does not catalyze hydrosilylation under atmospheric pressure and temperatures of 20—120°C. Catalysts of the cobalt triad are the most effective in hydrosilylation of olefins of higher nucleophilicity. In the case of olefins with electron with drawing substituents, e.g. acrylonitrile, hydrosilylation with dicobaltoctacarbonyl occurs only at room temperature over several days, the yields of hydrosilylation products do not exceed 20% [3].

TABLE 1

CONSTANTS AND ELEMENTAL ANALYSES OF PRODUCTS OF OLEFIN HYDROSILYLATION

No.	Compound	Yield (%)		B.p. (°C/ mmHg)	n_d^{20}	Found (%)			Empirical formula	Calcd. (%)		
		$Co_2\cdot(CO)_8$	$Rh_4\cdot(CO)_{12}$			C	H	Si		C	H	Si
I	$C_6H_5CH_2CH_2Si(OC_2H_5)_3$	91	94	130—131/2	1.3965	62.43	8.79	10.21	$C_{14}H_{24}O_3Si$	62.64	9.01	10.46
II	$(CH_3)_3SiCH_2CH_2Si(OC_2H_5)_3$	95	96	220—221/740	1.4123	50.60	10.60	21.10	$C_{11}H_{28}O_3Si_2$	50.0	10.60	21.20
III		35	50	202—205/10	1.4817	35.42	8.83	8.20	$C_{10}H_{30}B_{10}O_3Si$	35.85	8.97	8.39
IV		33	45	163—166/3	1.4961	37.65	8.66	8.10	$C_{11}H_{32}B_{10}O_3Si$	37.90	9.12	8.05
V	$(C_2H_5O)_3SiCH_2CH_2CH_2N$- $Si(OC_2H_5)_3)_2$	54	72	160—161/4	1.4225	48.32	9.54	10.24	$C_{21}H_{51}NO_9Si_2$	48.70	9.92	10.84
VI		93	95	208—210/740	1.4315	57.89	9.44	12.27	$C_{11}H_{22}O_3Si$	57.34	9.62	12.19
VI		91	93	165—166/740	1.4640	52.52	8.16	17.18	$C_7H_{13}ClSi$	52.31	8.15	17.47

Results and discussion

As the result of hydrosilylation of α-olefins, styrol, vinyltrimethylsilane and di-*N*-substituted allylamines with trichloro-, methyldichloro-, ethyldichloro-, dimethylchloro-, and triethoxy-silanes, in the presence of cobalt group carbonyls, isomers of normal structure are formed (eq. 1).

$$R'CH{=}CH_2 + HSiR''_nX_{3-n} \rightarrow \underset{(I,II)}{R'CH_2CH_2SiR''_nX_{3-n}} \qquad (1)$$

(I, $R' = C_6H_5$, $X = OC_2H_5$, $n = 0$; II, $R' = Si(CH_3)_3$, $X = OC_2H_5$, $n = 0$; $R' = C_3H_7$—$C_{10}H_{21}$, $R'' = CH_3$, C_2H_5, $X = Cl$, $n = 1, 2$; $X = Cl, OC_2H_5$, $n = 0$).

The structure of the products of hydrosilylation of α-olefins was determined using elemental analysis, mass, IR_c and NMR spectra; in the case of hydrosilylation with $HSi(OC_2H_5)_3$ VPC was also used (Table 1). IR spectra of reaction products do not show vinyl group valence vibrations bands; those of alkyltriethoxysilanes exhibit intense band at 1090 cm^{-1}, characteristic for C—O bond valence vibrations. More information on the structure of reaction products can be obtained from NMR spectra. These do not contain signals due to methyne protons which suggests an absence of branch chained alkylsilanes in the reaction products.

Contrary to some workers [1,2] it was found that catalytic addition of hydridesilanes to α-olefins occured readily at 40—50°C, (see Fig. 1).

However, olefins with electron with drawing substituents, e.g. alkenyl-*o*-carboranes, virtually do not undergo hydrosilylation at elevated temperature. In the presence of cobalt and rhodium carbonyls this process occurs only at room temperature (60 h, 20—35% yields) (eq. 2).

The reaction also proceeds at 0°C but a longer reaction time is required. Increasing the temperature badly reduces the reaction rate, thus on refluxing the reaction mixture hydrosilylation of alkenyl-*o*-carboranes does not practically proceed.

Otherwise hydrosilylation of olefins with higher nucleophilicity is accompanied by a violent heat evolution which essentially required cooling of the reac-

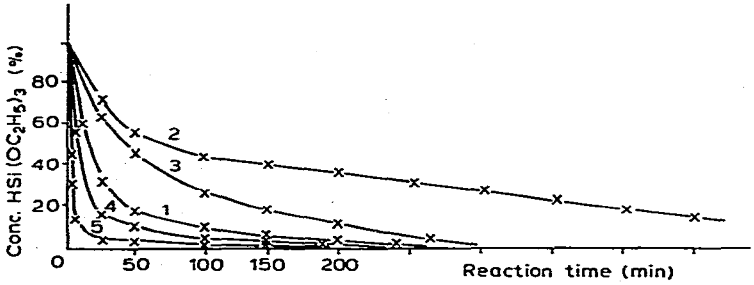
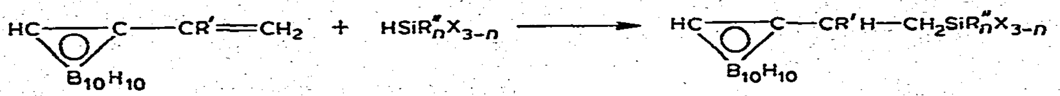


Fig. 1. Relative rates of triethoxysilane conversion on hydrosilylation using metal carbonyls as catalysts ($HSi(OC_2H_5)_3$: $CH_2{=}CHSi(CH_3)_3$ = I : I) 1, Concentration of $Co_2(CO)_8$, 0.023 *M*, temperature 30°C; 2, Concentration of $Co_2(CO)_8$, 0.012 *M*, temperature 30°C; 3, Concentration of $Co_2(CO)_8$, 0.012 *M*, temperature 40°C; 4, Concentration of $Co_2(CO)_8$, 0.012 *M*, temperature, 50°C; 5, Concentration of $Rh_4(CO)_{12}$, 0.0011 *M*, temperature 30°C.


(2)

(III, IV)

III, $R' = H, X = OC_2H_5, n = 0$; IV, $R' = CH_3, X = OC_2H_5, n = 0$

$R' = H, CH_3; R'' = CH_3, C_2H_5; X = Cl, n = 1,2; X = Cl, OC_2H_5, n = 0$

tion mixture. Thus, hydrosilylation of *N,N*-dimethylallylamine and *N,N*-bis(triethoxysilyl)allylamine can be carried out merely by stirring the reaction mixture with catalyst for several hours [6] (eq. 3). The reaction products always contain

$$CH_2{=}CH\text{-}CH_2NR_2 + HSi(OC_2H_5)_3 \rightarrow (C_2H_5O)_3SiCH_2CH_2CH_2NR_2 \quad (3)$$

(V)

(V, $R = Si(CH_3)_3$; $R = CH_3$)

a small amount of $Si(OC_2H_5)_4$; formed as the result of disproportionation of $HSi(OC_2H_5)_3$ in the basic medium.

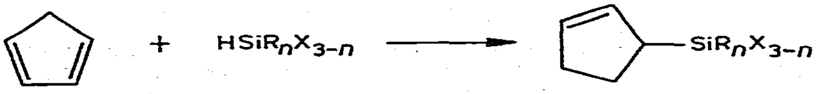
Hydrosilylation of allylamine is a more complex process. Cobalt and rhodium carbonyls catalyze addition of the silyl fragment to the amine group [7], analogously to H_2PtCl_6 [8]. However, unlike the latter, in the case of cobalt and rhodium carbonyls, silylation of the nitrogen atom is the initial step, and only subsequently does hydrosilylation of the double bond proceed. This fact was proved by studying the reaction of reagents with ratios $CH_2{=}CHCH_2NH_2/HSi(OC_2H_5)_3$ 1 : 1, 1 : 2, 1 : 3, and 1 : 4. In the first case only the product of silylation of the amine group, *N,N*-bis(triethoxysilyl)allylamine, was obtained (eq. 4). With a

$$CH_2{=}CH\text{-}CH_2NH_2 + 2\ HSi(OC_2H_5)_3 \rightarrow CH_2{=}CH\text{-}CH_2N[Si(OC_2H_5)_3]_2 \quad (4)$$

ratio 1 : 3 as well as with a greater excess of $HSi(OC_2H_5)_3$, the main reaction product is 1-triethoxysilyl-3-*N,N*-bis(triethoxysilyl)propylamine (V). In other cases a mixture of silylation products is formed. An excess of allylamine inhibits the reactions. In all the cases $Si(OC_2H_5)_4$ is obtained as a by-product.

Structures of the products were determined by elemental analysis, IR and NMR spectra (see Table 1). The IR spectrum of *N,N*-triethoxysilylallyamine shows an absorption band at 1660 cm^{-1}, ν(C=C), and does not contain the ν(NH) band (3560 cm^{-1}). The NMR spectrum of the compound exhibits 5 signals with the intensity ratio 18 : 2 : 12 : 1 : 2 (δ, ppm): triplet at 1.3 (CH_3) doublet at 1.8 (CH_2N), quadruplet at 3.7 (OCH_2), multiplet at 5.05 (CH), and doublet at 6.2 ($CH_2{=}$). NMR spectrum of 1-triethoxysilyl-3-*N,N*-bis(triethoxysilyl)propylamine (V) shows 5 signals with the intensity ratio 2 : 27 : 2 : 2 : 18 (δ, ppm): doublet at 0.85 (CH_2Si), triplet at 1.3 (CH_3), multiplet at 2.0 (CH_2N), triplet at 2.7 (CH_2), and quadruplet at 3.7 (OCH_2).

Cobalt and rhodium carbonyls effectively catalyze the addition of silanes, except trichlorosilane, to cyclopentadiene. In this case only one of the double bonds is attacked (eq. 5). The reaction is so violent that it is necessary to cool


(5)

(VI, VII)

VI, $X = OC_2H_5$, $n = 0$; VII, $R = CH_3$, $X = Cl$, $n = 2$

the reaction mixture. The reaction of $HSiCl_3$ with cyclopentadiene gave a resin even whilst cooling and no hydrosilylation products were isolated.

The pentenylsilanes VI, VII obtained, according to NMR spectral data, do not have the same structure. In cyclopentenyltriethoxysilane (VI) the triethoxysilyl group occupies an α-position to the double bond. The NMR spectrum of VI contains 6 signals with the intensity ratio 9 : 2 : 2 : 6 : 1 : 1 (δ, ppm): triplet at 1.23 (CH_3 of OC_2H_5 group), mutiplet at 1.9 (CH_2 of the nucleum), multiplet at 2.4 (CH_2 of the nucleum), quadruplet at 3.85 (OCH_2), doublet at 5.7 (=CH), and doublet at 6.3 (=CH). The NMR spectrum of cyclopentenyldimethylchlorosilane (VII) suggests a symmetrical structure; 3 signals with the intensity ratio 6 : 4 : 2 (δ, ppm): singlet at 0.4 (CH_3), multiplet at 2.4 (CH_2 of the nucleum) and multiplet at 5.7 (=CH).

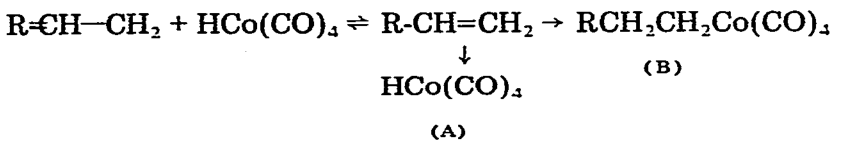
To study the influence of temperature, quantity and nature of catalyst on the rate of hydrosilylation the reaction of vinyltrimethylsilane with triethoxysilane was chosen as a model. As may be seen from Fig. 1, increasing the amount of cobalt carbonyl together with an increase in temperature up to 50°C sharply increases the hydrosilylation rate. Rhodium carbonyl, under similar reaction conditions is a more effective catalyst than that of the cobalt compound. The former catalyzes hydrosilylation so strongly that it is complete in several minutes after mixing the reagents.

The data cited allow some conclusions to be made on the mechanism of hydrosilylation in the presence of metal carbonyls. As in the Oxo synthesis, cobalt hydrocarbonyl ($HCo(CO)_4$), is the active intermediate catalytic group that forms in accordance with the eq. 6 [9]. It should be noted that catalysis with metal carbonyls occurs in an open system under atmospheric pressure, i.e. without substitution of carbonyl group, whereas catalysis with substitution of a carbonyl group requires at least a CO pressure of about 30 atm to regenerate catalyst.

$$HSiX_3 + Co_2(CO)_8 \rightarrow HCo(CO)_4 + Co(CO)_4SiX_3 \qquad (6)$$

A peculiarity of hydrosilylation of olefins containing electron-withdrawing substituents is the fact that the reaction proceeds only at lowered temperatures, which leads to the assumption that in the present case the intermediate $HCo(CO)_4 \cdot$ olefin (A) is formed (Scheme 1). These compounds are formed without substitution of CO, owing to the charge transfer from the olefin to the catalyst, their stability ensures successful hydrosilylation of olefins. Probably olefins with increasing nucleophilicity readily make π-complexes of type A stable at 40—50°C, whereas lowering the electron density of the double bond does not favour their formation. As a result of transfer of electron density from olefin to metal, redistribution of the density becomes possible in the metalhydridecarbonyl system together with an attack on the more electrophilic carbon atom of the double bond by the hydride atom of hydrogen, the complex A giving the σ-complex B.

SCHEME 1



$$R\text{-}CH{=}CH_2 + HCo(CO)_4 \rightleftharpoons \begin{array}{c} R\text{-}CH{=}CH_2 \\ \downarrow \\ HCo(CO)_4 \\ \text{(A)} \end{array} \rightarrow \begin{array}{c} RCH_2CH_2Co(CO)_4 \\ \text{(B)} \end{array}$$

This scheme explains not only the formation of only linear isomers, but also the peculiarity of the catalysis of olefins with different electron densities. In the case of olefins with increased electron density, intermediate complexes with the charge transferred are stable enough since more effective charge transfer takes place. This is the reason why these complexes are stable at elevated temperatures, and that catalytic hydrosilylation of α-olefins, vinyltrimethylsilane and substituted allylamines is possible even in refluxing reaction mixture. In the case of weak donors such as acrylonitrile and alkenyl-*o*-carboranes, complexes of catalysts with olefins are insufficiently stable, so that they are exputed to exist in a sufficient quantity at low temperatures. In this connection, hydrosilylation of these below 30°C proceeds only very slowly. With increasing temperature these complexes either do not form or dissociate before the transition of complex A into complex B. Formation of the final product and regeneration of catalyst could appear to involve a reaction of complex B with silane (eq. 7). Thus, according to the proposed reaction scheme, the principal stage of the process is the addition of hydrocarbonyl to olefin.

$$R{-}CH_2CH_2Co(CO)_4 + HSiX_3 \rightarrow R{-}CH_2CH_2SiX_3 + HCo(CO)_4 \qquad (7)$$

Experimental

IR spectra were recorded on UR-20 spectrometer with KBr, NaCl and LiBr prisms. NMR spectra were measured on T-60 A spectrometer, benzene was used as internal standard. Purity of starting and final products as well as the extent of reaction were monitored using GLC (120—170°C, column 2000 X 4 mm filled with Chromosorb W).

Since all α-olefins were hydrosilylated using the same method the synthesis of only one product is described.

Hexyltriethoxysilane

To a flask equipped with a stirrer, a condenser and thermometer 21.05 g (0.25 mol) of 1-hexene, 41.08 g (0.25 mol) of triethoxysilane and 0.62 g of $Co_2(CO)_8$ (or 0.062 g of $Rh_4(CO)_{12}$) were added, the mixture was stirred for 1 h at 35—40°C. Distillation gave 56.1 g (89%) of a colourless liquid hexyltriethoxysilane, b.p., 210—211°C/740 mmHg); n_d^{20}, 1.4168; d_4^{20}, 0.894. (Found: C, 58.37; H, 10.23; Si, 11.04. $C_{12}H_{28}O_3Si$ calcd.: C, 58.01; H, 11.36; Si, 11.30%.) IR spectrum (liq.): 2990 s, 2900s, 2750w, 1450, 1400s, 1300, 1100s, 970s, 800s, 680w, 480 cm^{-1}.

Alkyl(ethoxy)silanes with general formula $R'CH_2CH_2SiR''_nX_{3-n}$ ($R' = C_3H_7$—$C_{10}H_{21}$; $R'' = CH_3, C_2H_5, n = 1,2; X = Cl; n = 0, X = Cl, OC_2H_5$) were prepared analogously. Boiling points, refraction indexes, elemental analyses, IR and NMR spectra are identical with those cited in the literature [4,10].

1-Phenyl-2-triethoxysilylethane (I)

A mixture of 10.4 g (0.1 mol) of styrene, 16.4 g (0.1 mol) of triethoxysilane and 0.26 g of $Co_2(CO)_8$ (or 0.026 g of $Rh_4(CO)_{12}$) was stirred at 20—30°C for 70 h. Distillation afforded 24.4 g of a colourless liquid I (see Table 1). IR spectrum (liq.): 2980s, 2950, 2900, 1480w, 1450w, 1400, 1300, 1100s, 960s, 480w cm^{-1}. Compounds of general formular $R'CH_2CH_2SiR''_nX_{3-n}$ ($R' = C_6H_5$; $R'' = CH_3, C_2H_5$; $X = Cl$, $n = 1,2$; $n = 0$, $X = Cl, OC_2H_5$) were synthesized similarly and their analytical data were identical with that cited elsewhere [4,11].

1-Trimethylsilyl-2-triethoxysilylethane (II)

A mixture of 10.0 g (0.1 mol) of vinyltrimethylsilane, 16.4 g (0.1 mol) of triethoxysilane and 0.26 g of $Co_2(CO)_8$ (or 0.026 g of $Rh_4(CO)_{12}$) was stirred at 30—40°C for 1 h. Distillation of the mixture gave 25.1 g of a colourless liquid II (see Table 1). IR spectrum (liq.): 2980s, 2900, 1390s, 1250, 1180, 1100s, 980, 870, 790, 700w, 510, 420 cm^{-1}.

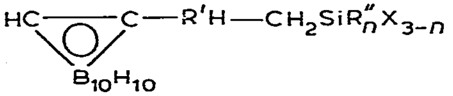
Compounds $R'CH_2CH_2SiR''_nX_{3-n}$ ($R' = Si(CH_3)_3$; $R'' = CH_3, C_2H_5$, $X = Cl$, $n = 1,2$; $n = 0$, $X = Cl, OC_2H_5$) were obtained analogously. Analytical data for these compounds are identical with those cited in the literature [4,5].

1-o-Carboranyl-2-triethoxysilylethane (III)

A mixture of 5.1 g (0.03 mol) of 1-vinyl-*o*-carborane, 16.4 g (0.1 mol) of triethoxysilane and 0.21 g of $Co_2(CO)_8$ (or 0.021 g of $Rh_4(CO)_{12}$) was stirred at 20—30°C for 60 h. Distillation gave 3.5 g of a colourless liquid III (see Table 1). IR spectrum (liq.): 3100s, 2900, 1400, 1250s, 1080s, 1050s, 830s, 750s, 700s, 650, 470 cm^{-1}.

2-o-Carboranyl-3-triethoxysilylpropane (IV)

As described above, from 5.55 g (0.03 mol) of isopropenyl-*o*-carborane, 16.4 g (0.1 mol) of triethoxysilane and 0.21 g of $Co_2(CO)_8$ (or 0.021 g of $Rh_4(CO)_{12}$), 3.1 g of a colourless liquid IV was obtained (see Table 1). IR spectrum (liq.): 3100s, 2990s, 2800s, 2600s, 1630s, 1440s, 1370s, 1300, 1200, 1020s, 920s, 890, 800, 730s, 560w, 480 cm^{-1}.

Compounds of general formula  $\underset{B_{10}H_{10}}{HC{-}C}{-}R'H{-}CH_2SiR''_nX_{3-n}$ ($R' = H, CH_3$; $R'' = CH_3, C_2H_5$, $X = Cl$, $n = 1,2$; $n = 0$, $X = Cl, OC_2H_5$) were prepared in a similar way (lit. [4,12].)

1-Triethoxysilyl-3-N,N-dimethylpropylamine.

A mixture of 32.8 g (0.2 mol) of triethoxysilane, 8.6 g (0.1 mol) of *N,N*-dimethylallylamine and 0.25 g of $Co_2(CO)_8$ (or 0.025 g of $Rh_4(CO)_{12}$) was stirred at room temperature for 5 h. Subsequent distillation afforded 21.4 g (86% with respect to *N,N*-dimethylallylamine) of 1-triethoxysilyl-3-*N,N*-dimethylpropylamine, a colourless liquid, b.p., 75—78°C/2 mmHg; n_d^{20}, 1.4985, (lit. [13]: b.p., 45°C/0.25 mmHg; n_d^{20}, 1.5007.), together with 9.0 g of tetraethoxysilane.

1-Triethoxysilyl-3-N,N-bis(triethoxysilyl)propylamine(V)

(*a*) As described above, from 32.8 g (0.2 mol) of triethoxysilane, 38.16 g (0.1 mol) of *N,N*-bis(triethoxysilyl)allylamine and 0.25 g of $Co_2(CO)_8$ (or 0.025 g of $Rh_4(CO_{12})$, 43.0 g (83% with respect to the amine) of compound V was prepared (see Table 1) together with 8.0 g of tetraethoxysilane.

(*b*) As described, from 49.4 g (0.3 mol) of triethoxysilane, 5.7 g (0.1 mol) of allylamine and 0.55 g of $Co_2(CO)_8$ (or 0.055 g of $Rh_4(CO)_{12}$), 29.5 g of a colourless liquid V (see Table 1) and 18 g of tetraethoxysilane were obtained. IR spectrum of V (liq.): 2990s, 29290s, 2900s, 1490w, 1450, 1400s, 1370, 1300, 1100s, 800s, 690, 480s cm^{-1}.

Hydrosilylation of other derivatives of allylamine was carried out similarly.

N,N-Bis(triethoxysilyl)allylamine

Following the above method (twice distilling), from 32.8 g (0.2 mol) of triethoxysilane, 11.4 g (0.2 mol) of allylamine and 0.44 g of $Co_2(CO)_8$ (or 0.044 g of $Rh_4(CO)_{12}$) 29.1 g (60%) of *N,N*-bis(triethoxysilyl)allylamine was prepared as a colourless liquid, b.p., 60—62°C/1 mmHg n_d^{20}, 1.4132. IR spectrum (liq.): 3000s, 2920, 2900s, 1680, 1450w, 1400, 1300w, 1230w, 1170s, 1100s, 970s, 800s, 710w, 480 cm^{-1}.

Cyclopentenyltriethoxysilane (VI)

A mixture of 32.8 g (0.2 mol) triethoxysilane, 13.2 g (0.2 mol) of cyclopentadiene and 0.46 g of $Co_2(CO)_8$ (or 0.046 g of $Rh_4(CO)_{12}$) was stirred at 30—35°C for 1 h. Distillation of the mixture gave 42.8 g of a colourless liquid VI (see Table 1). IR spectrum (liq.): 2900 s, 2920s, 2900s, 1600, 1450, 1400s, 1300, 1180s, 1100s, 950s, 780s, 700, 560s, 480 cm^{-1}.

Cyclopentenyl(dimethyl)chlorosilane (VII)

As described for VI, from 18.93 g (0.2 mol) of dimethylchlorosilane, 13.2 g (0.2 mol) of cyclopentadiene and 0.32 g of $Co_2(CO)_8$ (or 0.032 g of $Rh_4(CO)_{12}$) 29.4 g of a colourless liquid VII was prepared, (see Table 1). IR spectrum (liq.): 3050s, 2980s, 2950s, 2900s, 2850s, 1630, 1450, 1410, 1260s, 1050s, 920s, 820s, 680s, 600, 480s cm^{-1}.

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