

• Synthesis of Aliphatic-Aromatic Silanes and
Their Dehydrogenation

77355
SOV/79-30-1-16/78

products. Work dealing with the selection of the catalysts for dehydrogenation of aliphatic-aromatic silanes is being continued. The authors express their gratitude to T. K. Lavrovskaya for analysis of gases. There are 10 references, 6 Soviet, 2 German, 2 U.S. The U.S. references are: Hurd, D., J. Am. Chem. Soc., 67, 1545 (1945); Roland, P., Marquardt, K., Luce, E. W., Anal. Chem., 23, 629 (1951).

ASSOCIATION: N. D. Zelinskiy Institute of Organic Chemistry of the Academy of Sciences of the USSR (Institut organicheskoy khimii imeni N. D. Zelinskogo AN SSSR)

SUBMITTED: January 21, 1959

Card 4/4

5.3600

77855
SOV/79-30-2-6/78

AUTHORS: Petrov, A. D., Chernyshev, Ye. A., Dolgaya, M. Ye.,
Yegorov, Yu. P., ~~Leytes, L. A.~~

TITLE: Addition of Silanes to Alkenylbenzenes in the Presence
of Chloroplatinic Acid

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 2, pp 376-
383 (USSR)

ABSTRACT: The authors effected addition of trichlorosilane and
alkyldichlorosilanes to styrene, allylbenzene, and γ -
butenylbenzene by using chloroplatinic acid as a
catalyst (1 ml of 0.1 M solution in isopropyl alcohol
per 1.2 mole each of silane and alkenylbenzene. The
reaction was performed at 30-40°, in a four-neck round-
bottom flask, provided with a stirrer, reflux condenser,
thermometer, and a dropping funnel (for slow and con-
tinuous addition of the alkenylbenzene). While addi-
tion of trichlorosilane results in only one product,
the methyl- and ethyldichlorosilanes produce two isomers
each:

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Addition of Silanes to Alkenylbenzenes in the Presence of Chloroplatinic Acid

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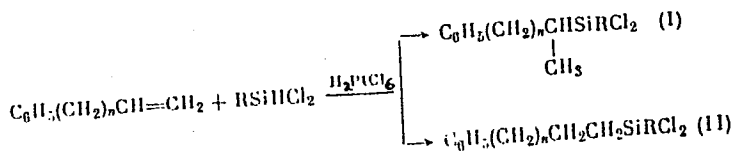
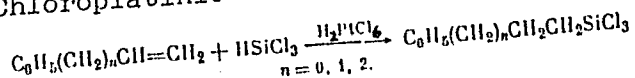


Table A lists the synthesized compounds and their properties. The reaction of obtained compounds with $MgCH_3Br$ and $MgCH_3CH_2Br$ led to formation of trialkylphenylalkylsilanes: δ -phenylbutyltrimethylsilane (bp $91-92^\circ$ (3 mm), n_D^{20} 1.4828, d_4^{20} 0.8656); γ -phenylpropyltrimethylsilane (bp 56° (2 mm), n_D^{20} 1.4853, d_4^{20} 0.8684); γ -phenylpropyltriethylsilane (bp 165° (20 mm), n_D^{20} 1.4949, d_4^{20} 0.8939); δ -

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Table A.

1	2	3	4	5	n _D ²⁰	d ₄ ²⁰	MR _D		6 M _D				8	7 M _D			
							6	7	с	н	я	а		с	н	я	а
HSiCl ₃	C ₈ H ₇ CH=CH ₂	C ₈ H ₇ CH ₂ CH ₂ SiCl ₃ 9	61.8	79.25	1.5184	1.2386	58.59	58.01	-	-	-	-	C ₈ H ₇ SiCl ₃	-	-	-	-
HSiCl ₃	C ₈ H ₇ CH=CH ₂	C ₈ H ₇ CH ₂ CH ₂ CH ₂ SiCl ₃ 10	42.4	110 (10)	1.5140	1.2239	62.32	62.67	42.55	4.13	11.13	41.66	C ₈ H ₁₁ SiCl ₃	42.62	4.31	11.06	41.97
HSiCl ₃	C ₈ H ₇ CH=CH ₂	C ₈ H ₇ CH ₂ CH ₂ CH ₂ CH ₂ SiCl ₃ 11	24.3	117 (6)	1.5114	1.1957	67.07	67.30	-	-	-	-	C ₁₀ H ₁₃ SiCl ₃	-	-	-	-
		C ₈ H ₇ CHSiCl ₂ CH ₂ CH ₃ 12	12.9	61 (2)	1.5183	1.1361	58.14	58.41	-	-	-	-	C ₉ H ₁₀ SiCl ₃	-	-	-	-
CH ₃ SiHCl ₂	C ₈ H ₇ CH=CH ₂	C ₈ H ₇ CH ₂ CH ₂ SiCl ₂ CH ₃ 13	50.0	68 (2)	1.5120	1.1311	58.10	58.51	-	-	-	-	C ₈ H ₁₀ SiCl ₂	-	-	-	-
		C ₈ H ₇ CH ₂ CHSiCl ₂ CH ₃ CH ₃ 14	7.5	101.5 (9)	1.5152	1.1165	62.78	63.04	-	-	-	-	C ₁₀ H ₁₁ SiCl ₂	-	-	-	-
CH ₃ SiHCl ₂	C ₈ H ₇ CH=CH ₂	C ₈ H ₇ CH ₂ CH ₂ CH ₂ SiCl ₂ CH ₃ 15	50	119.5 (9)	1.5102	1.1050	62.83	63.04	-	-	-	-	C ₁₀ H ₁₁ SiCl ₂	-	-	-	-

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Table A. (Cont'd.)

$C_8H_9SiHCl_2$	$C_8H_7CH_2CH_2CH=CH_2$	$C_8H_7CH_2CH_2CH_2CH_2SiCl_2CH_3$ 16	9.7	111.5 (6)	1.5124	1.0970	67.81	67.47	53.51, 53.36	6.45, 6.50	11.10, 11.30	28.65, 28.50	$C_{11}H_{16}SiCl_2$	53.46	6.47	11.34	28.71
$C_8H_9SiHCl_2$	$C_8H_7CH_2CH_2CH=CH_2$	$C_8H_7CH_2CH_2CH_2CH_2SiCl_2CH_3$ 17	61.9	129-130 (10)	1.5067	1.0925	67.25	67.47	53.59, 53.63	6.37, 6.36	11.20, 11.36	28.39, 28.39	$C_{11}H_{16}SiCl_2$	53.46	6.47	11.34	28.71
$C_8H_9SiHCl_2$	$C_8H_7CH=CH_2$	$C_8H_7CH_2CH_2CH_2CH_2$ 18	18.3	88(7)	1.5160	1.1218	62.73	63.04	51.55, 51.71	6.05, 6.07	12.26, 12.12	30.27, 30.17	$C_{10}H_{14}SiCl_2$	51.52	6.01	12.02	30.44
$C_8H_9SiHCl_2$	$C_8H_7CH=CH_2$	$C_8H_7CH_2CH_2SiCl_2C_2H_5$ 19	40.3	106 (4)	1.5095	1.1149	62.45	63.01	52.11, 52.30	6.16, 6.15	11.27, 11.17	29.65, 29.55	$C_{10}H_{14}SiCl_2$	51.52	6.01	12.02	30.44
$C_8H_9SiHCl_2$	$C_8H_7CH_2CH=CH_2$	$C_8H_7CH_2CH_2SiCl_2C_2H_5$ 20	8.0	105 (5)	1.5160	1.1060	67.13	67.67	53.62, 53.60	6.44, 6.35	11.61, 11.55	28.83, 28.59	$C_{11}H_{16}SiCl_2$	53.46	6.47	11.34	27.71
$C_8H_9SiHCl_2$	$C_8H_7CH_2CH=CH_2$	$C_8H_7CH_2CH_2CH_2SiCl_2C_2H_5$ 21	57.0	114 (5)	1.5103	1.0993	67.23	67.67	—	—	—	—	$C_{11}H_{16}SiCl_2$	—	—	—	—
$C_8H_9SiHCl_2$	$C_8H_7CH_2CH=CH_2$	$C_8H_7CH_2CH_2CH_2SiCl_2C_2H_5$ 22	9.2	124 (7)	1.5135	1.0833	72.16	72.30	55.21, 55.33	6.78, 6.89	10.42, 10.48	26.98, 27.16	$C_{12}H_{18}SiCl_2$	55.19	6.89	10.73	26.78
$C_8H_9SiHCl_2$	$C_8H_7CH_2CH_2CH=CH_2$	$C_8H_7CH_2CH_2CH_2CH_2SiCl_2C_2H_5$ 23	61.0	147.5 (6)	1.5078	1.0837	71.79	72.30	55.27, 55.32	6.89, 6.93	10.47, 10.59	27.45, 27.30	$C_{12}H_{18}SiCl_2$	55.19	6.89	10.73	26.79

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the Presence of Chloroplatinic Acid

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Key to Table A: (1) Chlorosilane; (2) aromatic compound;
(3) synthesized compound; (4) yield based on chloro-
silane (in %); (5) boiling point (pressure in mm); (6)
found; (7) calculated; (8) empirical formula; (9) β -
phenylethyltrichlorosilane; (10) γ -phenylpropyltri-
chlorosilane; (11) δ -phenylbutyltrichlorosilane; (12)
 α, α -phenylmethylmethylmethylmethylmethylmethylmethyl-
phenylethylmethylmethylmethylmethylmethylmethyl-
dichlorosilane; (13) β -
benzylmethylmethylmethylmethylmethylmethyl-
dichlorosilane; (14) α, α -methyl-
dichlorosilane; (15) γ -phenylpropylmethyl-
dichlorosilane; (16) α, α -Methyl- β -phenylethylmethyl-
dichlorosilane; (17) δ -phenylbutylmethylmethylmethyl-
(18) α, α -methylphenylethyldichlorosilane; (19) β -
phenylethylethyldichlorosilane; (20) α, α -methylben-
zylethyldichlorosilane; (21) γ -phenylpropylethyl-
dichlorosilane; (22) α, α -methyl- β -phenylethyl-
dichlorosilane; (23) δ -phenylbutylethyldichlorosilane.

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phenylbutyltriethylsilane (bp 106° (2 mm), n_D^{20} 1.4922, d_4^{20} 0.8862). Raman spectra of all the listed compounds (and 4 other derivatives) were taken. The spectra of alkenylbenzenes with straight ($\geq S_1(CH_2)_n C_6H_5$, $n = 1, 2, 3, 4$) and branched ($\geq SiCH(CH_3)(CH_2)_n C_6H_5$, $n = 0, 1, 2$) chains show a marked difference which can help differentiate between the two types. The compounds containing straight chain alkyl groups have two lines ($\sim 1,185$ and $\sim 1,207$ cm^{-1}) in the region 1,180-1,210 cm^{-1} , whose frequency and intensity do not depend upon the length of the chain. The compounds of the second type show only one line in this region, whose frequency and intensity depend upon the value of n . Increase in n lowers the frequency and raises the intensity of the line. There are 1 table; and 7 references, 2 Soviet, 1 Japanese, 4 U.S. The U.S. references are: C. A. Burkhard, R. H. Krieble, J. Am. Chem. Soc., 69, 2687 (1947); Ch. A., 49, 14377 (1955); G. H. Wagner,

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Addition of Silanes to Alkenylbenzenes in
the Presence of Chloroplatinic Acid

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D. L. Bailey, A. N. Pines, et al., Ind. Eng. Ch., 45,
367 (1953); J. H. Speier, J. A. Webster, G. Barnes,
J. Am. Chem. Soc., 79, 974 (1957).

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March 2, 1959

Card 7/7

81705

S/020/60/132/05/35/069
B011/B126

5.3700(B)

AUTHORS: Petrov, A. D., Corresponding Member AS USSR,
Chernyshev, Ye. A., Li Guan-lian

TITLE: The Interaction of Silicon Hydrides With α - and β -Chloro-naphthalene and With p-Dichlorobenzene. The Pyrolysis of Ethyl Chlorosilanes in the Presence of Arylchlorides

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 5, pp. 1099 - 1102

TEXT: The authors studied the condensation of the above compounds at high temperature. The possibility of the formation of p-bis-(trichlorosilyl)-benzene and its analogues on the basis of Scheme A, and of phenyldichlorosilane from ethyldichlorosilane and chlorobenzene on the basis of Scheme B, was established. The influence of the temperature of the reaction zone on the degree of conversion of silicon-hydride, and the yield of the reaction products for α -chloronaphthalene were examined. Figs. 1 and 2 show the results ($\tau = 30$ sec). In the case of chloronaphthalene, a parallel reaction of naphthalene and silicontetra-

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81705

The Interaction of Silicon Hydrides With α - and β -Chloronaphthalene and With p-Dichlorobenzene. S/020/60/132/05/35/069
The Pyrolysis of Ethyl Chlorosilanes in the Presence of Arylchlorides BO11/B126

chloride (or methyltrichlorosilane) (II) takes place (as with other arylchlorides) beside the formation of naphthylsilanochloride. The silicon hydrides react with chloronaphthalenes at a lower temperature than with chlorobenzene. Reaction I prevails over reaction II (Table 1). The highest yields of naphthylchlorosilanes were obtained with both α - and β -chloronaphthalene at 640°. The yield of β -naphthylmethylchlorosilane was 41%, and that of β -naphthyltrichlorosilane was 51%. The naphthylchlorosilanes obtained were methylated by CH_3MgBr . The yield and physical data of the products obtained are given. It follows from the absorption spectra that, when α -chloronaphthalene is used, only α -naphthylchlorosilane is produced, and when β -chloronaphthalene is used, only β -naphthylchlorosilane is produced. Thus, no isomerization of chloronaphthalene takes place. Its interaction with silicon hydrides occurs on the C-Cl bond. The reaction of silicon hydrides with p-dichlorobenzene in benzene medium was carried out under different ratios of the components. The reaction products and the yields are given. The bis-(chlorosilyl)-benzenes obtained were methylated, and have shown

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B011/B126

The Interaction of Silicon Hydrides With α - and β -Chloronaphthalene and With p-Dichlorobenzene.
The Pyrolysis of Ethyl Chlorosilanes in the Presence of Arylchlorides

themselves to be identical on the use of both HSiCl_3 and $\text{CH}_3\text{SiHCl}_2$. Thus the reaction occurs also in this case only on the C-Cl bond, and without isomerization (Table 1). The products obtained are explained by pyrolytic decomposition of ethyldichlorosilane above 550°C , and by the reaction of the resulting radicals (Table 2). Chlorobenzene reacts with ethyltrichlorosilane and diethyldichlorosilane as well. 29% phenyltri-chlorosilane and 5% phenyldichlorosilane respectively, and 6% phenyl-ethyldichlorosilane and 5% diphenyldichlorosilane were formed. 21% α -naphthylethyldichlorosilane and some 30% α -naphthyltrichlorosilane were formed from the reaction of ethyldichlorosilane with α -chloro-naphthalene (1 : 2). There are 2 figures, 2 tables, and 5 references: 4 Soviet and 2 British.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Insti-
tute of Organic Chemistry of the Academy of Sciences,
USSR)

SUBMITTED: February 26, 1960

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PHASE I BOOK EXPLOITATION

807/5606

Petrov, Aleksandr Dmitriyevich, Vladimir Florovich Mironov, Vasilii Andreyevich Ponomarenko, and Yevgeniy Andreyevich Chernyshev

Sintez kremniyorganicheskikh monomerov (Synthesis of Organosilicon Monomers)
Moscow, Izd-vo AN SSSR, 1961. 550 p. Errata slip inserted. 4,500 copies printed.

Sponsoring Agency: Akademiya nauk SSSR. Institut organicheskoy khimii im. N. D. Zelinskogo.

Resp. Ed.: A. V. Topchiyev, Academician; Ed. of Publishing House: I. S. Povarov;
Tech. Eds.: V. G. Laut and I. A. Streletskiy.

PURPOSE: This book is intended for chemists and graduate students of chemistry and related fields and may be used as a handbook by engineers interested in the synthesis and properties of polymeric materials.

COVERAGE: The book gives the results of the authors' research on the synthesis of monomeric organosilicon compounds and reviews data published through 1960

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80V/5606

Synthesis of Organosilicon Monomers

on methods of synthesis and properties of the more important and widely used organosilicon monomers. The Introduction and Chs. I, II, and IV were written by A. D. Petrov; Ch. III and Part III by Ye. A. Chernyshev; Ch. V, jointly by Chernyshev and Mironov; Part II by V. F. Mironov; and Part IV by V. A. Ponomarenko. The Conclusion was written by Petrov, Mironov, and Chernyshev. The authors thank R. Kh. Freydina, Corresponding Member, AS USSR, and M. G. Voronkov, Candidate of Chemical Sciences. There are 142 references: 92 Soviet, 44 English, 1 Italian, 2 French, and 3 German.

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S/661/61/000/006/025/081
D205/D302

AUTHORS: Chernyshev, Ye. A., Mironov, V. F. and Petrov, A. D.

TITLE: Relative reactivity of carbofunctional silico-organic compounds with functional groups in the α -, β - and γ -position with respect to the silicon atom

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh soyedineniy; trudy konferentsii, no. 6, Doklady, diskussii, resheniye. II Vses. konfer. po khimii i prakt. prim. kremneorg. soyed., Len. 1958. Leningrad. Izd-vo AN SSSR, 1961, 119-122

TEXT: The influence of the position of the functional group was studied in three series of compounds: $\text{>Si} - (\text{CH}_2)_n\text{Cl}$ (I), $\text{>Si}(\text{CH}_2)_n\text{CH} = \text{CH}_2$ (II) and $\text{>Si}(\text{CH}_2)_n\text{C}_6\text{H}_5$ (III). In compounds of type (I) and (III) the reactivity is always influenced by nucleophilic reagents in the same manner: The most reactive are the β -compounds, ✓

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D205/D302

Relative reactivity of ...

then the α -compounds and the γ -compounds in this order. By action of electrophilic reagents another reactivity series of the compounds was observed: $\beta > \gamma > \alpha$. This is also true for silico-olefines. In radical reactions the reactivity sequence of the compounds is $\alpha > \gamma > \beta$. This behavior indicates a conjugation effect between the Si-C bond and the functional group. This effect is confirmed also by a series of physical features of the compounds having the functional group in the β -position. The magnitude of the conjugation effect depends on the other groups or atoms bonded to the silicon atom. In usual conditions it is impossible to perform the addition of CCl_4 , CHCl_3 , HSiCl_3 or aldehydes to $\text{R}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ while the same addition to $\text{Cl}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ proceeds easily. Thus, the conjugation effect is almost non-existent in the latter case. A. L. Klebanskiy (VNIISK, Leningrad), Ya. I. Mindlin (Moscow) and R. Kh. Freydlina (INEOS AN SSSR, Moscow) took part in the discussion, its main theme being the nature of the effect between the substituents in the α -, β - and γ -positions and the Si atom. ✓

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Relative reactivity of ...

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D205/D302

ASSOCIATION: Institut organicheskoy khimii AN SSSR, Moskva (In-
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Card 3/3

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5.3700

2900, 1164, 1273

20940

S/062/61/000/003/006/013
B117/B208

AUTHORS: Yegorov, Yu. P., Leytas, L. A., Tolstikova, N. G.,
Chernyshev, Ye. A.

TITLE: Spectroscopic investigation of the effect of the silicon atom
on multiple bonds in molecules of organosilicon compounds

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, no. 3, 1961, 445-454

TEXT: The present paper continues a previous study (Ref. 1: A. D. Petrov,
Yu. P. Yegorov, V. F. Mironov, G. I. Nikishin, A. A. Bugorkova, Izv.
AN SSSR. Otd. khim. n. 1956, 50; Ref. 2: Yu. P. Yegorov, Ye. A. Chernyshev,
Materialy X Vsesoyuznogo soveshchaniya po spektroskopii, Izv. L'vovskogo
gos. un-ta t. 1, 1957, str. 390) on physical and chemical properties of
organosilicon compounds with multiple bonds in different positions to the
silicon atom. In particular, some para-substituted benzene derivatives
with β and γ positions of the silicon atom to the aromatic ring were
studied. The Raman spectra of the following compounds were taken:

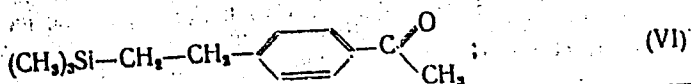
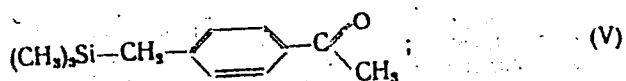
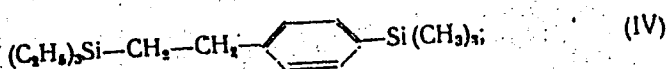
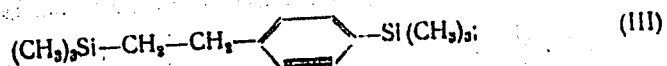
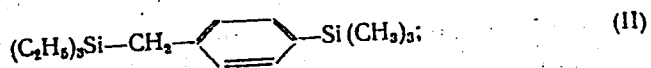
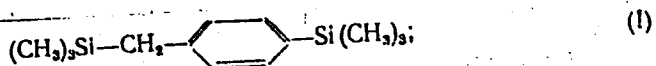
Card 1/6

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S/062/61/000/003/006/013
B117/B208

Spectroscopic investigation of the...



Card 2/6

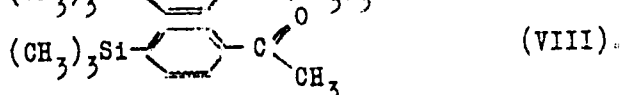
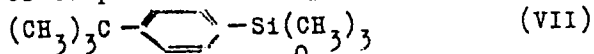
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B117/B208

Spectroscopic investigation of the...

Furthermore, the ultrared spectra were taken of compounds (I), (III), (V), (VI), as well as of compounds with α -position of silicon to the ring



p-trimethyl-silyl-tert-butyl benzene was obtained from p-chloro-tert-butyl benzene and trimethyl chloro silane by the reaction of Würtz-Fittig, and p-tri-methyl-silyl-triethyl- β -phenyl-ethyl silane by the Grignard reaction. All other silicon hydrocarbons were also prepared in tetrahydrofuran under the same conditions. Properties and yields of the resultant compounds are given in Table 5. Silicon-containing aromatic ketones were obtained by a method described in Ref. 19 (Ye. A. Chernyshev, E. N. Klyukina, A. D. Petrov, Izv. AN SSSR. Otd. khim. n. 1960, 1601). The Raman spectra were taken with an $\omega\text{C}\beta$ -51 (ISP-51) device. The line intensity in the maximum was measured photometrically with a cyclohexane scale and by the method of the internal standard (CCl_4 was used as internal standard). An anomalous reactivity, as compared to compounds with α and

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Spectroscopic investigation of the...

positions of the silicon atom, was observed in compounds with β -position of the silicon atom to the ring. The intensity of the lines assigned to symmetric vibrations of the system $\rightarrow \text{Si} - \text{C} - \text{C} - \text{X}$ in the Raman spectrum increases. In ultraviolet spectra recorded with an CF_4 (SF-4) spectrophotometer, an increase in intensity and a bathochromic band shift is observable. The exaltation of MR_D (molecular refraction) increases. In systems $\rightarrow \text{Si} - \text{C} - \text{C} = \text{C}$ and $\rightarrow \text{Si} - \text{C} - \text{C} - \text{X}$, a specific mutual influence between the multiple bonds or the aromatic ring and the complicated electron shell of the silicon atom in the valence state occurs. This effect is possibly enhanced by the steric configuration of the system $\text{Si} - \text{C} - \text{C} - \text{X}$. As may be seen from the models by Stuart and Brigleb,

1 2 3 4
a structure is possible in these systems with the atoms 1 and 4 located so closely that van der Waal's radii overlap each other. Conclusions on this effect in compounds of different series may be drawn only after further studies of the line intensities and chemical properties. Mention is made of Ye. A. Chernyshev, M. Ye. Dolgaya, A. D. Petrov, V. M. Tatevskiy, P. P. Shorygin, B. A. Kazanskiy, V. T. Aleksanyan. There are 2 figures, 5 tables, and 19 references: 14 Soviet-bloc and 5 non-Soviet-bloc.

Card 4/6

Spectroscopic investigation of the...

S/062/61/000/003/006/013
B117/B208

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo
Akademii nauk SSSR (Institute of Organic Chemistry imeni
N. D. Zelinskiy, Academy of Sciences USSR)

SUBMITTED: December 1, 1959

a. C_6H_4 Соединение	Выход, % b. (6)	Т. кип., °C (мм рт. ст.) c. (2)	n_D^{20}	d_4^{20}
$(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{C}_6\text{H}_4-\text{Si}(\text{CH}_3)_3$	84	85-80 (4)	1,4911	0,8681
$(\text{CH}_3)_3\text{Si}-\text{C}_6\text{H}_4-\text{CH}_2-\text{Si}(\text{CH}_3)_3$	80	110-112 (5)	1,4788	0,8668
$(\text{C}_2\text{H}_5)_3\text{Si}-\text{CH}_2-\text{C}_6\text{H}_4-\text{Si}(\text{CH}_3)_3$	71	130-132 (6)	1,4990	0,8842
$(\text{C}_2\text{H}_5)_3\text{Si}-\text{CH}_2-\text{C}_6\text{H}_4-\text{Si}(\text{CH}_3)_3$	78	139 (3)	1,4939	0,8877

Card 5/6

Table 5

S/062/61/000/003/007/013
B117/B208

AUTHORS: Chernyshev, Ye. A. and Tolstikova, N. G.
TITLE: Hammett constants of some trialkyl silyl alkyl groups
PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, no. 3, 1961, 455-459

TEXT: The authors characterized quantitatively the nature of some tri-alkyl silyl alkyl groups by means of their Hammett constants σ^- and σ^+ . To calculate these constants, the dissociation constants of a number of p-trialkyl silyl alkyl-substituted derivatives of aromatic acids, and the ionization constants of analogous amines were determined. The method of obtaining para-substituted silicon-containing benzoic acids and anilines has been previously described (Ref. 21: Ye. A. Chernyshev, N. G. Tolstikova, Zh. obshch. khimii 31, 1961). The apparent dissociation constants were determined by potentiometric titration at $25.0 \pm 0.1^\circ\text{C}$. Hydrogen ion concentration was measured with glass and calomel electrodes (with a saturated KCl solution) on an Mn-5 (LP-5) tube potentiometer. The calculated constants σ^- and σ^+ of a number of $\text{R}_3\text{Si}(\text{CH}_2)_n$ groups are presented in

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S/062/61/000/003/007/013
B117/B208

Hammett constants of some...

Table 3. This table also gives the Hammett constants of $(\text{CH}_3)_3\text{Si}-$, $(\text{C}_2\text{H}_5)_3\text{Si}-$, $(\text{C}_6\text{H}_5)_3\text{Si}-$ groups taken from publications or calculated from them. These data substantiate the specific effect of the silyl group on the aromatic ring in β -position to the silicon atom. The decisive effect of the character of the remaining three atoms or radicals bound to the silicon atom on the intensity of this effect and the specific behavior of β -functional organosilicon compounds, which are known by the collective term " β -effect", indicate the following: One of the principal causes of σ - σ - or σ - π conjugation is the steric factor of the positions of silicon and X-atom of the system $\text{Si}-\underset{1}{\text{C}}-\underset{2}{\text{C}}-\underset{3}{\text{C}}-\underset{4}{\text{X}}$. Considering the models by Stuart and Brigleb for several organosilicon compounds, it may be concluded that the silicon atom greatly affects the bonds being in 3-4 position to it by its electron shell. These bonds are considerably polarized, which causes their anomalous reactivity with respect to the neighboring homologs. There are 5 tables and 21 references: 9 Soviet-bloc and 12 non-Soviet-bloc. The 2 references to English-language publications read as follows: L. Hammett, Physical Organic Chemistry, N. Y., 1941; H. H. Jaffe, Chem.

Card 2/4

Hammett constants of some...

S/062/61/000/003/007/013
B117/B208

Rev. 53, 191, 1953.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, Academy of Sciences USSR)

SUBMITTED: January 6, 1960

Table 3: Hammett constants of some silyl groups. Legend: a) consecutive numbers; b) silyl group; c) σ^- para; d) σ^- meta; e) σ^+ para; f) σ^+ meta;

g) Refs.: The references to English language publications read as follows: ✓
Ref. 12: J. Chatt, A. A. Williams, J. Chem. Soc. 1954, 4403; Ref. 13:
R. A. Benkeser, H. R. Krysiak, J. Amer. Chem. Soc. 75, 2421, 1953; Ref. 18:
J. D. Roberts, C. M. Regan, J. Amer. Chem. Soc. 75, 4102, 1953; Ref. 19:
R. A. Benkeser, C. E. deBoer, R. E. Robinson, D. M. Sauve, J. Amer. Chem. Soc. 78, 682, 1956; Ref. 20: C. Eaborn, S. H. Parker, J. Chem. Soc. 1954, 939. The Hammett constants indicated by an asterisk were determined by the authors of this paper.

Card 3/A1
3

27498
S/062/61/000/009/014/014
B117/B101

S-3700

AUTHORS:

Chernyshev, Ye. A., Dolgaya, M. Ye., and Petrov, A. D.

TITLE:

Synthesis and properties of aryl-fluoro silicon hydrides

PERIODICAL:

Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 9, 1961, 1718

TEXT: This "Letter to the Editor" describes a new simple method for the preparation of a type of silicon hydrides. Aryl-fluoro silicon hydrides are obtained by treating the corresponding aryl-chloro silicon hydrides with concentrated hydrofluoric acid at -30° - 50° C:
 $R_nCl_{3-n}SiH + (3-n)HF \rightarrow R_nF_{3-n}SiH + (3-n)HCl$. The time of contact of the reactants is 20-30 min. Products having only one chlorine atom substituted by fluorine may be obtained by shortening the time of contact. The yields of aryl-fluoro silicon hydrides are 70-90%. Under the influence of water, alcohols, and acids, without a catalyst, aryl-fluoro silicon hydrides split off hydrogen, even at room temperature, and form silanol, alkoxy and acyloxy silane derivatives, respectively. Formation of hydrogen at the

Card 1/2

30165

S/062/61/000/012/004/012
B118/B147

5-3700
AUTHORS:

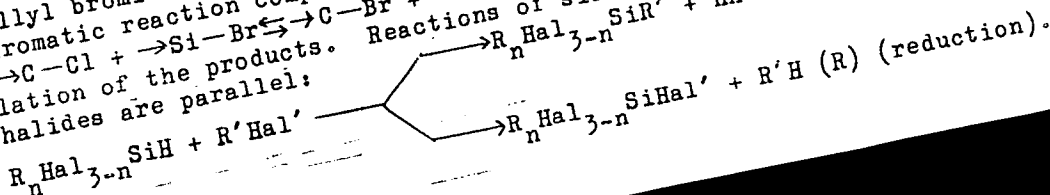
Chernyshev, Ye. A., Tolstikova, N. G., and Bugerenko, Ye. F.

TITLE:

Interaction of silicon bromo- and silicon chloro-hydrides with some organobromides and alkyl chloro benzenes in the gaseous phase

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 12, 1961, 2173 - 2178

TEXT: Based on a paper by A. D. Petrov, Ye. A. Chernyshev, and Li Kuang-liang (Dokl. AN SSSR, 137, 876 (1961)), the authors studied the reaction of tribromosilane with bromo benzene, α -bromo naphthalene, and allyl bromide. Instead of aryl chlorides they used aryl bromides as aromatic reaction component to avoid the conversion $\rightarrow C-Cl + \rightarrow Si-Br \rightleftharpoons \rightarrow C-Br + \rightarrow Si-Cl$ which would involve difficult isomerization of the products. Reactions of silicon halo-hydrides and organohalides are parallel:



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B' 18/B147

Interaction of silicon...

The aim of the present study was the determination of the ratio C/R. Replacement of chlorine atoms by bromine in silicon halo-hydride was found to support the condensation reaction. Besides electronegativity, the steric factor (volume) of atoms or groups bound to Si in silicon hydride, and possibly also the structure of their electron shells, have an effect upon the ratio C/R. At 580°C and 30 sec contact with chloro benzene, HSiCl_3 yields 70 - 75% of the final product, whereas HSiBr_3 yields 98 - 99%. A 60% yield of α -naphthyl tribromosilane is obtained by reaction between $\alpha\text{-C}_{10}\text{H}_7\text{Br}$ and HSiBr_3 . The yields of phenyl and allyl tribromosilanes were only 17.5 and 12.5%, respectively. The authors also converted trichloro silane and methyl-dichloro silane with chlorotoluenes, chloro-ethyl benzenes, chloro-isopropyl benzenes, and p-chloro-tert-butyl benzene in the gaseous phase at high temperature. The syntheses of tolyl-, ethyl-, phenyl-, and isopropyl-phenyl chloro silanes at high temperature (600°C) and in the gaseous phase were compared with the known conversions of silicon chloro-hydrides with alkyl benzenes or alkyl chloro benzenes in the liquid phase. In all cases of this comparison, the ratios of ortho-isomers, meta-isomers and para-isomers of alkyl phenyl-trichloro silanes

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Interaction of silicon...

S/062/61/000/012/004/012
B118/B147

and alkyl phenyl methyl-dichloro silanes, according to Raman-spectrum analytical data, were almost the same as those of the initial alkyl chloro benzenes. In Table 2, the reaction of silicon hydrides with aryl chlorides in the gaseous phase is compared with that of silicon hydrides with alkyl benzenes in the liquid phase. A considerable residue which, according to elementary analysis, contains silicon and hydrolyzable chlorine besides carbon and hydrogen, is obtained on interaction of silicon hydrides and alkyl chloro benzenes in the gaseous phase at a temperature above 600 - 620°C. The authors thank L. A. Leytes for his spectrum analysis. There are 3 tables and 10 references: 8 Soviet and 2 non-Soviet. The reference to the English-language publication reads as follows: A. Barry, I. W. Gilkey, D. E. Hook, *Industr. and Engen. Chem.* 51, 91 (1959).

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: June 22, 1961

Card 3/0 3

PETROV, A.D.; PLATE, A.F.; CHERNYSHEV, Ye.A.; DOLGAYA, M. Ye.; BELIKOVA, N.A.;
KRASNOVA, T.L.; LEYTES, L.A.; PRYANISHNIKOVA, M.A.; TAYTS, G.S.;
KOZYRKIN, B.I.

Preparation of organosilicon derivatives of bicyclo [2.2.1]
heptane. Zhur. ob. khim. 31 no.4:1199-1208 Ap '61. (MIRA 14:4)

1. Institut organicheskoy khimii Akademii nauk SSSR.
(Bicycloheptane) (Silicon organic compounds)

25B00

S/080/61/034/002/022/025
A057/A129

15.8100

AUTHORS: Chernyshev, Ya.A., Mironov, Y.F., Nepoznina, V.V.,
Lisgunov, S.A.

TITLE: Reaction of silicon hydrides with ethyl- and isopropyl-
benzene and preparation of trichlorosilyl-substituted styrenes

PERIODICAL: Zhurnal Prikladnoy Khimii, v 34, no 7, 1961, 458-460

TEXT: Arylsilanes were synthesized by reactions of trichloro-
silane and methylchlorosilane with ethylphenyl- and isopropylphenyl-
benzenes in liquid phase under pressure using H_2SO_4 as catalyst. Methyl-
dichlorosilane was more active than trichlorosilane. Trichlorosilyl-sub-
stituted styrene and *o*-methylstyrene was obtained by chlorination of
ethylphenyl- and isopropylphenyltrichlorosilanes to monochlorides, and
pyrolysis of the latter. Nowadays three syntheses of arylchlorosilanes
are frequently studied. The most developed is the method studied in the

Card 1/5

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25800

S/080/61/034/002/022/025
A057/A:29

Reaction of silicon hydrides ...

present investigation, i.e., the reaction between silicon hydride and benzene (or homologs) in liquid phase under pressure at 200°-400°C with catalysts (BCl_3 , H_2BO_3 , AlCl_3 , etc.). In the second method instead of benzene (or homologs) an arylhalide is used (Ref 7: A. Barry et al., Ind. Eng. Chem., 51, 91 (1959)) and twice as much silicon hydride is necessary than in the first method. In the third variant silicon hydride and arylhalide react in gaseous phase at atmospheric pressure in flowing systems at 500°-700°C (Ref 8: Ya.A. Chernyshev et al., DAN SSSR, 127, 808 (1959), Ref 9: ibid. 132, 1099 (1960), Ref 10: A.D. Petrov et al., ibid. 126, 1009 (1959), Ref 11: V.A. Ponomarenko et al., ibid. 130, 333 (1960)). The present experiments were carried out to compare the yields of the arylchlorosilanes and to check results of other investigators. The reaction occurred in a rotating steel autoclave (1 l), ratio of components was 1 : 1 with 0.1 weight % of catalyst and contact time of 5 hrs at varying temperatures from 230°-380°C. The results (Fig.) indicate the higher activity of methylchlorosilane in comparison to trichlorosilane. This is in agreement with observations in Ref 7, but differs from the statement

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Reaction of silicon hydrides

25400
S/080/61/034/002/022/025,
A057/A129

given by N. N. Tishina et al. (Ref. 5: "Khimiya i prakticheskoye primeneniye kremneorganicheskikh soyedineniy" ("Chemistry and practical use of siliconorganic compounds"), I., Izd. TsBTI, L. 91 (1958)) that H_2BO_3 has no catalytic activity for reactions between trichlorosilane and benzene. Spectral analysis demonstrated that the obtained arylchlorosilanes contained: 10 - 20 % ortho-, 40 - 60 % meta- and 30 - 40 % para-isomers. Characteristics of the obtained arylchlorosilanes are presented in the Table. Chlorination and pyrolysis of the arylchlorosilanes to styrenes were carried out by methods developed by D. W. Lewis (Ref. 12: J. Org. Chem., 23, 1893 (1958)). At the present time the authors investigate the third method of arylchlorosilane synthesis to compare the yields of the three methods. There is 1 figure, 1 table and 12 references: 10 Soviet-bloc and 2 non-Soviet-bloc.

SUBMITTED: May 11, 1960

Card 3/5

3

21498

S/020/61/137/004/022/031
B103/B208

5.3700

2209, 1164, 1273

AUTHORS:

Petrov, A.D., Corresponding Member AS USSR,
Chernyshev, Ye.A. and Li Kuang-liang

TITLE:

Mechanism of interaction of silicon hydrides with
organohalides in the gaseous phase

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 4, 1961, 876 - 879

TEXT: The authors have previously found that the reaction

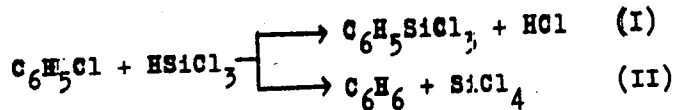
$$R_n Cl_{3-n} SiH + R'Cl \rightarrow R_n Cl_{3-n} SiR' + R_n Cl_{4-n} Si + R'H + HCl$$
 proceeds nearly quantitatively (Ref. 1, DAN, 127, 808, 1909, where also the methods are described). Therefore, they studied the material balance of the following reactions at 580°C and atmospheric pressure: (Table 1) (I) chloro-benzene with trichloro-silane, (II) o-chloro-toluene with trichloro-silane, and (III) chloro-benzene with methyl-dichloro-silane. The gaseous reaction products account for 1 - 2 wt%. As no secondary reactions took place, the authors concluded that the interaction in this case proceeds in two parallel directions, as, for instance, in case (I):

Card 1/a
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B103/B208

Mechanism of interaction of ...



Reaction (I) is called

condensation (cond), reaction (II) reduction (red). The cond/red ratio was studied in reactions of trichloro-silane with 18 organohalides (Table 2). The molar quantity of the resultant organotrichloro-silane characterizes the condensation product, and that of silicon tetrachloride the reduction product. It is concluded from Table 2 that cond/red in aromatic organochlorides is determined by two factors: a) by the nature of the substituent, and b) by steric hindrances. Cond/red is also considerably affected by the nature of the halogen in the organohalide. If chlorine is replaced by bromine or fluorine, cond/red decreases. Also the nature of the silicon hydride exerts a considerable effect on cond/red. It may be seen from Table 3 that by substituting alkyl or aryl radicals for chlorine atoms in trichloro-silane, the reduction is increased with increasing substitution of chlorine atoms. The homolytic character of the discussed reaction has earlier been confirmed (Ref. 1 et al.). The present results elucidated its mechanism. Here, radicals were obviously formed by thermal

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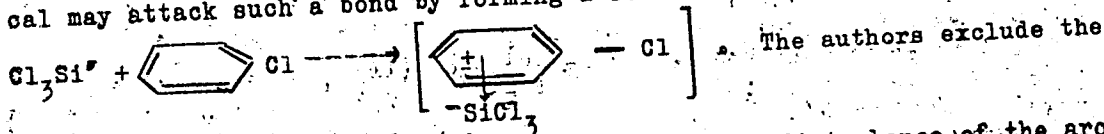
21498

S/020/64/137/004/022/031
B103/B208

Mechanism of interaction of ...

dissociation of the Si - H bonds: $\text{HSiCl}_3 \rightarrow \dot{\text{H}} + \dot{\text{SiCl}}_3$. This was exemplified by reaction (I) (Table 1). It was concluded that the silyl radical $\dot{\text{SiCl}}_3$ is the effective agent in the course of the process. The two reactions (cond and red) are evidently the result of an attack of this radical on the organochloride molecule, but at two different points. The following reaction scheme is assumed: $\text{C}_6\text{H}_5\text{Cl} + \dot{\text{SiCl}}_3 \rightarrow \text{SiCl}_4 + \text{C}_6\text{H}_5\dot{\text{C}}$

$\text{C}_6\text{H}_5 + \text{HSiCl}_3 \rightarrow \text{C}_6\text{H}_6 + \text{SiCl}_3$. To render the condensation reaction possible, the C-Cl bond in the organochloride must be located at a carbon atom combined with the adjacent carbon atom by a π bond. The silyl radical may attack such a bond by forming a so-called π -complex, such as



possibility of intermediate σ -complexes and of a disturbance of the aromatic system. Interaction of the intermediate π -complex with the tri-

Card 3/R

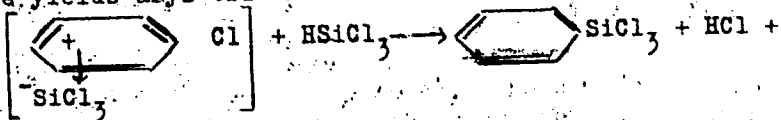
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B103/B208

Mechanism of interaction of ...

chloro-silane molecule yields aryl trichloro-silane and HCl, with a silyl radical being formed



+ $\cdot\text{SiCl}_3$. The authors summarize that the condensation and reduction mechanisms are characterized by the competition of the silyl radical attack against: A) the chlorine atom, and B) the π -electron bond of the organochloride molecule. This hypothesis of the mechanisms of the condensation and reduction reactions might be a satisfactory explanation of the results, a) the increase of the cond/red ratios by electron donor substituents in chloro-benzene, b) the decrease of cond/red by an electron acceptor in the same compound, c) the increase of cond/red in the reaction with chloro-naphthalenes, d) the occurrence of the reduction reaction alone (cond/red = 0) in saturated aliphatic chlorides. There are 3 tables and 13 Soviet-bloc references.

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5

Mechanism of interaction of ...

S/020/61/137/004/022/051
B103/B208

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR
(Institute of Organic Chemistry of the Academy of
Sciences USSR)

SUBMITTED: December 26, 1960

Legend to Table 1:

1) reaction, 2) initial compounds, 3) resultant compounds. The values
in the numerator denote the quantities in millimoles, and in the denomi-
nator in grams.

Card 5/8
5

29015

S/020/61/140/004/016, 23
B106/B110

5 3700
AUTHORS:

Petrov, A. D., Corresponding Member AS USSR, Chernyshev, Ye.
A and Krasnova, T. L.

TITLE:

Synthesis of silicon-, germanium-, and tin-containing
parasubstituted styrenes and α -methyl styrenes

PERIODICAL:

Akademiya nauk SSSR. Doklady, v. 140, no. 4, 1961, 837-840

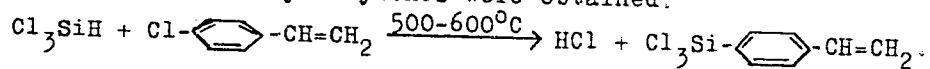
TEXT: Silicon-, germanium-, and tin-substituted styrenes were synthesized by a method devised by H. Normant (Ref. 20: C. R., 239, 1510 (1954)) for the synthesis of organomagnesium compounds, as modified by J. R. Leebrick and H. E. Ramsden (Ref. 15: J. Org. Chem., 23, 935 (1958)), for the synthesis of other elemental-organic compounds. Moreover, the authors used a method of synthesis recently developed by themselves and based on high-temperature condensation of p-chloro styrene with silicon hydrides (Ref. 21: Ye. A. Chernyshev, Li Guam-lian, A. D. Petrov, DAN, 127, 808 (1959); Ref. 22: Ye. A. Chernyshev, V. F. Mironov, A. D. Petrov, Izv. AN SSSR, OKhN, 1960, 2147). For the first time p-triethyl-silyl, p-tri-t-butyl-germyl, and p-triethyl-stannyl styrenes were obtained by the authors

29015

Synthesis of silicon-, germanium-, ...

S/O20/61/140/004/016/023
B106/B110

by the Normant-Ramsden method. If the vacuum is not high enough, a considerable part of these styrenes polymerizes in the distilling flask. Silicon-substituted styrenes with functional groups (halogens or alkoxy groups) on the heteroatom are very interesting since these compounds can be converted to polymers both by polymerization at the styrene double bond and by hydrolysis of the M-Hal or M-OR bonds with subsequent polycondensation (M meaning heteroelement). Up to now, monomers of this type had been obtained merely by pyrolysis of chloro-alkyl-phenyl chloro silanes. Moreover, styryl chloro silanes proved to be obtainable by reacting p-vinyl-phenyl magnesium chloride with silicon tetrachloride, methyl trichlorosilane, and dimethyl dichlorosilane. Yields exceed 50%. Formulas, properties, and analytical data of heteroelement-containing styrenes obtained by the Normant-Ramsden method are given in Table 1. p-chloro styrene or p-chloro- α -methyl styrene were used as aromatic component for syntheses by the authors' new method. Thus, chlorosilyl styrenes and α -methyl chlorosilyl styrenes were obtained:



Results obtained are shown in Table 2. It is interesting that neither

Card 2/5 3

29015 .

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B106/B110

Synthesis of silicon-, germanium-,...

silicon tetrachloride, nor methyl trichlorosilane, nor reduction products of styrene or α -methyl styrene could be isolated from the reaction mixture, when trichlorosilane and methyl dichlorosilane were reacted with p-chloro styrene and p-chloro- α -methyl styrene. It is presumed that mainly condensations and no reductions occur at the high temperatures involved. There are 2 tables and 23 references: 12 Soviet-bloc and 11 non-Soviet-bloc. The three most recent references to English-language publications read as follows: A. E. Senear, J. Wirth, R. G. Neville, J. Org. Chem., 25, 807, (1960); D. W. Lewis, J. Org. Chem., 23, 1893 (1958); H. G. Pars, W. A. Graham, E. R. Atkinson, C. R. Morgan, Chem. and Ind., No. 24, 693 (1960).

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: April 29, 1961

Card 3/3

3

S/062/62/000/007/005/013
B117/B180

AUTHORS: Chernyshev, Ye. A., and Tolstikova, N. G.
TITLE: Reaction of chlorosilanes with alkyl benzenes and α - and β -chlorostyrenes in the gas phase
PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 7, 1962, 1223 - 1228

TEXT: The authors examined the assumption that the reaction of chlorosilanes with alkyl chlorobenzenes above 650°C takes place not only via the C-Cl bond of the latter, but also via C-H and C-C bonds. Using the reaction of trichlorosilane with alkyl benzenes (toluene; p-, m-, o-xylene, diphenyl methane, and ethyl benzene). It was found that the aromatic hydrocarbons mainly react via the C_{aryl}-C_{alkyl} bond. This reaction, in which the alkyl radical is substituted by trichlorosilyl groups, may pass through an intermediary stage of the π -complex, thus representing a new kind of homolytic substitution in the aromatic series. The formation of α - and β -trichlorostyrene (yields up to 60 - 75%) during the reaction of trichlorosilane with ethyl benzene was demonstrated by high-temperature

Card 1/2

Reaction of chlorosilanes with...

S/062/62/000/007/005/013
B117/B180

condensation. The high efficiency of high-temperature condensation was also confirmed by high yields (50 - 60%) of the reaction of α - and β -chloro chlorostyrene with methyl dichlorosilane.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: February 2, 1962

Card 2/2

CHERNYSHEV, Ye. R.

Z/009/62/000/008/001/002
E112/E435

AUTHORS: Setínek, Karel, Černyšev, J.A.

TITLE: Thermal decomposition of trichlorosilane

PERIODICAL: Chemický průmysl, no.8, 1962, 419-422

TEXT: The pyrolysis of SiHCl_3 was studied in a silica tube packed with crushed silicate glass at 525, 550, 600 and 750°C, partial SiHCl_3 pressures of 0.1 to 0.5 atm and flow rates of 10 to 70 mole/hour per 1 litre of reaction space. The products of thermal decomposition were identified by gas chromatography, using nitrogen as carrier gas and thermal conductivity as method of detection. Trichlorosilane was found to be stable at 525°C. Decomposition began at 550°C, giving rise to tetrachlorosilane and hydrogen. A solid decomposition product was also detected in minute quantities, collecting on the walls of the silica tube and over the silicate packing. A quantitative analysis of the solid substance was not undertaken because the collected quantities were insufficient. Analyses of the gaseous decomposition product under varying experimental conditions are presented in the form of graphs. The rate of decomposition of SiHCl_3 increases
Card 1/3 ✓

Z/009/62/000/008/001/002
E112/E435

Thermal decomposition of ...

with temperature. However, during the initial stages of decomposition, pyrolysis proceeded at a considerably diminished rate. Therefore, it is postulated that the solid pyrolytic decomposition products may catalyze the thermal decomposition, and that the smooth non-contaminated walls of the silica tube may inhibit it. To clarify the effects of surface characteristics on the course of SiHCl_3 -decomposition, a series of experiments were carried out in which the surface areas within the silica tube were varied by varying the granular diameters of the silicate packing. Although the effect of the clean non-contaminated wall surface was again clearly discernible, influences of surface areas or characteristics were not detected. It was confirmed that smooth and clean wall-surfaces inhibit the decomposition of trichlorosilane. However, as soon as the walls of the silica tube are coated with a thin film of the solid decomposition product, the cause of inhibition is removed and pyrolysis proceeds entirely in the gaseous phase. Stoichiometrically, the pyrolysis of SiHCl_3 was assumed to proceed according to equation:

$$4\text{SiHCl}_3 = \text{Si} + 3\text{SiCl}_4 + 2\text{H}_2$$

Although analyses of the decomposition products showed agreement with the above equation in Card 2/3

Thermal decomposition of ...

Z/009/62/000/008/001/002
E112/E435

most cases, it was impossible to establish a simple kinetic relationship corresponding to all determined values of the analyses. Decomposition of SiHCl_3 appears to be far more complex and proceeds by a series of disproportionation reactions. There are 5 figures and 2 tables.

ASSOCIATIONS: Ústav teoretických základů chemické techniky ČSAV, Praha (Institute of Basic Chemical Techniques, ČSAV, Prague) K. Setinek;
Ústav organické chemie AV SSSR, Moskva
(Institute of Organic Chemistry AS USSR, Moscow)

SUBMITTED: March 13, 1962

Card 3/3

SOLODOVNIKOV, S.P.; CHERNYSHEV, Ye.A.

Electron paramagnetic resonance spectra of anions of elements-substituted aromatic compounds. Part 1: Electron paramagnetic resonance spectra of anions of trialkylsilylbenzenes and trialkylsilylalkylbenzenes. Zhur.strukt.khim. 3 no.6:665-668 '62.
(MIRA 15:12)

1. Institut khimicheskoy fiziki AN SSSR i Institut organicheskoy khimii AN SSSR.
(Silicon organic compounds--Spectra) (Benzene)

33926

S/079/62/032/001/002/016
D205/D302

5.3700

AUTHORS: Chernyshev, Ye.A., and Vangnits, Ye.V.

TITLE: Interaction of silanes with aromatic compounds in liquid phase in the presence of boron trichloride

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 1, 1962, 24 - 29

TEXT: The reaction between silanes and aromatic compounds in the presence of catalysts of the Lewis acid type was investigated to explore its potentialities for preparing silicoorganic compounds containing polycyclic aromatic radicals and also two silyl substituents in the aromatic ring. The reactants were heated with 1 % BCl_3 for 6 hours at 300°C in a 1 l. steel rotating autoclave. After cooling, the residual pressure was 30 atm. Interaction of diphenyl (1 part) with trichlorosilane (2 parts) at 300°C in the presence of BCl_3 gave a 28.5 % yield of monosilyl substitutes and 7.6 % yield of disilyl substitutes. The 1 : 4 respective ratio of reactants gave a 31.2 % yield on monosilyl and 20.7 % of the disilyl substitu-.
Card 1/4

33926

S/079/62/032/001/002/016
D205/D302

Interaction of silanes with ...

tes. The crystalline monosilyl derivatives were methylated to liquid xenyl trimethylsilanes, for which the silylation, as shown by the infra-red spectra, was ~50 % in the meta- and ~50 % in the para-position. It was also determined spectrally that two trichlorosilyl groups are bonded to different rings of the diphenyl molecule. Terphenyl could not be reacted under any conditions. m-Diphenylbenzene could, however, be reacted with a yield of 3.3 and 7.5 % with trichlorosilane and methyldichlorosilane respectively. The reaction of benzene with trichlorosilane in 1 : 4 ratio in conditions similar to those of the diphenyl reaction gave 44.8 % of phenyltrichlorosilane and 9.2 % hexachloro-disilyl benzene. The twofold decrease in the yield of disilyl substitutes as compared with the diphenyl reaction is explained by the reduction in the reactivity of the ring caused by introduction of the electronegative trichlorosilyl group into the benzene molecule. The second silyl group in the diphenyl enters the second ring where the influence of the first silyl group is much weaker. The reaction of trichlorosilane (2 parts) with phenyltrichlorosilane (1 part) at 300°C gave a 18.3 % yield of hexachlorodisilylbenzene. At the same ratio of methyldichlorosilane

Card 2/4

33926

S/079/62/032/001/002/016

D205/D302

Interaction of silanes with ...

with phenylmethyldichlorosilane, the yield of bis-(methyldichlorosilyl)-benzene was 11 %. Spectral analysis of both products showed that they were mainly the meta-isomers. This formation of mainly meta-isomers is attributed to the activity of the electrophilic siliconium ions Cl_2Si^+ , considered to be higher than that of the carbonium ions which are the most active of the previously investigated electrophilic particles. The meta-isomer can also be formed by secondary processes. Thus, when heated at 250°C in the presence of BCl_3 and traces of HSiCl_3 , p-tolymethyldichlorosilane was isomerized in 50 % yield to the meta-isomer. The nature of the substituents has a bearing on the velocity of the reaction. The relative reactivities of benzene and toluene in the reaction were determined by using an equimolar mixture of benzene, toluene and trichlorosilane. At 250°C during 8 hours, the benzene reacted in 33 % and the toluene in 42 % yields. Thus, the introduction of an electron donor substituent activates the ring, while the introduction of an electron acceptor substituent passivates the ring. The experimental data, therefore, suggest an electrophilic mechanism. There are 1 table

Card 3/4

Interaction of silanes with ...

33926
S/079/62/032/001/002/016
D205/D302

and 9 references: 7 Soviet-bloc and 2 non-Soviet-bloc. The references to the English-language publications read as follows: A. Barry, I.W. Gilkey and D.E. Hook, Ind. Eng. Chem., 51, 291, 1959; H.C. Brown, and K.L. Nelson, J. Am. Chem. Soc., 75, 6292, 1953.

ASSOCIATION: Institut organicheskoy khimii im. N.D. Zelinskogo Akademii Nauk SSSR i Moskovskiy khimiko-tekhnologicheskiy institut im. D.I. Mendeleyeva (Institute of Organic Chemistry, im. N.D. Zelinskiy, AS USSR and Moscow Institute of Chemical Technology im. I.D. Mendeleev) ✓

SUBMITTED: January 2, 1961

Card 4/4

S/079/62/032/002/001/011
D204/D503

AUTHORS: Chernyshev, Ye., A., Tolstikova, N.G., Ioffe, S.L. and
Petrov, A.D.

TITLE: Interaction of disilanes with chlorobenzene in the vapor
phase

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 2, 1962, 369-374

TEXT: A continuation of earlier work concerned with the preparation of organochlorosilanes. In the present paper the authors describe the reactions of chlorobenzene with hexamethyl -, pentamethyl chloro-, tetramethyl dichloro- and hexachlorodisilanes. The reactions were studied by passing mixtures of PhCl (2 moles) and the corresponding disilane (1 mole) through a silica tube at 500-600°C. The reagents were in the hot zone for 30-35 secs. The products were then condensed and analyzed. Full experimental details are given. The interaction of PhCl with hexamethyl disilane at 500 and 550°C yielded $(\text{CH}_3)_3\text{SiCl}$, C_6H_6 , $(\text{CH}_3)_3\text{Si}\cdot\text{CH}_2\cdot\text{Si}(\text{CH}_3)_2\text{Cl}$

Card 1/3

S/079/62/032/002/001/011
D204/D303

Interaction of disilanes ...

and $C_6H_5 \cdot C_6H_5$. Small quantities of $Cl(CH_3)_2Si \cdot CH_2 \cdot Si(CH_3)_2Cl$ and $(CH_3)_3SiC_6H_5$ were also formed at $600^\circ C$. The reaction with pentamethyl chloro-disilane gave $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, C_6H_6 , $Cl(CH_3)_2Si \cdot CH_2 \cdot Si(CH_3)_2Cl$, $Cl(CH_3)_2Si \cdot CH_2 \cdot Si(CH_3)Cl_2$, $(CH_3)_3SiC_6H_5$, $Cl(CH_3)_2SiC_6H_5$ and $C_6H_5 \cdot C_6H_5$.

No thermal rearrangement of pentamethyl chloro-disilane was observed, in contrast to the hexamethyl disilane. The action of $PhCl$ on tetra methyl dichlorodisilane (at $600^\circ C$ only) resulted in $(CH_3)_2SiCl_2$, C_6H_6 , $Cl(CH_3)_2Si \cdot CH_2 \cdot Si(CH_3)Cl_2$, $Cl(CH_3)_2SiC_6H_5$ and $C_6H_5 \cdot C_6H_5$. In addition to the

above listed compounds, high-boiling residues were formed in the 3 cases. The nature of the products obtained is discussed and it is concluded that these reactions proceed by a free radical chain mechanism. The interactions begin with a displacement of an H-atom in the disilane by a silyl or a phenyl radical, followed by rearrangement of $\rightarrow Si \cdot Si \cdot CH_2$ into

$\rightarrow Si-CH_2-\dot{Si}$. The interaction, at $580^\circ C$, of $PhCl$ with

Card 2/3

Interaction of disilanes ...

S/079/62/032/002/001/011
D204/D303

hexachlorodisilane gave SiCl_4 , $\text{C}_6\text{H}_5\text{SiCl}_3$ and a high-boiling residue. This reaction is also thought to proceed by a radical mechanism. The preparation of hexamethyl - and hexachlorodisilanes is described. The other 2 disilanes were prepared from the hexamethyl disilane by the method of Kumada et al (Ref. 6: J. Org. Chem. 21, 1264 (1956)). L.A. Leytes helped the authors with spectral analysis of the products. There are 5 tables and 8 references: 3 Soviet-bloc and 5 non-Soviet-bloc. The 4 most recent references to the English-language publications read as follows: K.Shina and M.Kumada, J.Org.Ch., 23, 139 (1958); M.Kumada, M.Jamaguchi, J.Jamamoto, J. Nakajima and K. Shina, ibid., 21, 1264, (1956); H.P. Brown and C.W.A. Fowles, J.Chem. Soc., 1958, 2811; M.Kumada, J.Nakajima, M.Ichikawa and J. Jamamoto, J.Org. Ch., 23, 292, (1958).

ASSOCIATION: Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry im.N.D.Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: February 6, 1961

Card 3/3

S/080/62/035/004/014/022
D247/D301

5.2400

AUTHORS: Chernyshev, Ye. A., Dolgaya, M. Ye. and Li Kuang-Liang

TITLE: The effect of the material of the reaction vessel on the reaction between hydrogen silanes and chlorobenzene in the gaseous phase

PERIODICAL: Zhurnal prikladnoy khimii, v. 35, no. 4, 1962, 860-863

TEXT: Experiments were run with trichlorosilane and methyldichlorosilane with chlorobenzene in stainless steel, Armco-iron and ceramics at a temperature of 580°C and a reaction time of 30 seconds. The products were collected after cooling and were analyzed. The yields and the ratios of the products resulting from a condensation mechanism to those resulting from reduction were recorded. Similar yields and ratios for apparatus made from quartz and copper were given. It was suggested that sorption of the aryl halide on to iron of nickel surfaces was the factor favoring the reduction process. There are 1 figure and 8 Soviet-bloc references.

SUBMITTED: June 30, 1961
Card 1/1

3661E

S/020/62/143/004/016/027
B106/B138

15.817.

AUTHORS:

Bugezenko, Ye. F., Chernyshev, Ye. A., and Petrov, A. D.,
Corresponding Member AS USSR

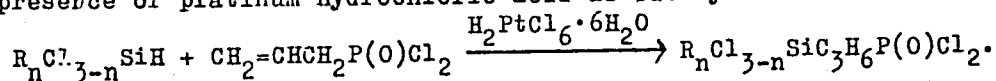
TITLE:

Synthesis of some organosilicon monomers with phosphorus-
containing functional groups

PERIODICAL:

Akademiya nauk SSSR. Doklady, v. 143, no. 4, 1962, 840-843

TEXT: A new method was worked out for synthesizing acid chlorides of organo chloro silyl alkyl phosphinic acids basing on the addition of organochloro-silicon hydrides to allyl phosphinic acid chloride in the presence of platinum hydrochloric acid as catalyst:



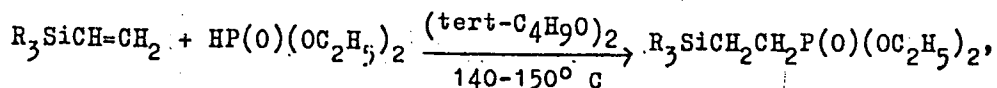
Trichloro-silane, methyl dichloro-silane, and ethyl dichlorosilane were used as silicon hydrides. Table 1 gives data on the resulting compounds (preparations III-V). Reaction conditions: 0.39 moles of the

Card 1/4

Synthesis of some organosilicon ...

S/020/62/143/004/016/027
B106/B138

organochloro-silicon hydride was slowly added to a mixture of 0.25 moles of allyl phosphinic acid chloride and 2 ml of a 0.1 M solution of platinum hydrochloric acid in isopropyl alcohol. The reaction was highly exothermic. The rate of addition of organo chloro silane was regulated so that the temperature did not exceed 50°C. After the addition, the reaction mixture was kept at 40°C (compound III), 60-65°C (compound IV), or 60-100°C (compound V), respectively for 2 hr. The products were isolated by distillation. With triethyl silane as starting material the reaction failed; nor was the addition of chlorosilanes to vinyl phosphinic acid chloride possible. Two ethyl esters of β-triorganosilyl ethyl phosphinic acids (preparations I, II in Table 1) were synthesized by adding dialkyl phosphinic acids to olefins (according to Ref. 2: R. G. Linville, US pat. 2843615 (1958); Chem. Abstr., 53, 1147 (1959); Ref. 5: G. H. Barnes, M. P. David, J. Org. Chem., 25, 1191 (1960)):



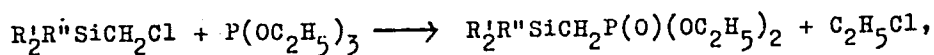
Card 2/5

X

Synthesis of some organosilicon ...

S/020/62/143/004/016/027.
B106/B138

(R = C₂H₅; -OC₂H₅). The small yield in the case of preparation II was due to the considerable polymerization of the initial triethoxy-vinyl silane during the reaction. Four new diethyl esters of triorganosilyl methyl phosphinic acids (preparations VI-IX) were synthesized by Arbuzov rearrangement (according to Ref. 1: A. R. Gilbert, US pat. 2768193 (1956); Chem. Abstr., 51, 5816 (1957)):



(R' = CH₃; R'' = C₂H₅, OC₂H₅; OSi(CH₃)₂CH₂Cl). Substitution of an ethyl

radical of the chloromethyl triorganosilane by the ethoxy radical considerably facilitates the rearrangement. The compounds synthesized in this work are of particular interest as monomers for the production of phosphorus -containing silicones, and also as lubricating oils, plasticizers, and insecticides. There is 1 table. The three most important English-language references are: W. H. Keeber, H. W. Post, J. Org. Chem., 21, 509 (1956); Fekete Frank, US pat. 2920094 (1960);

Card 3/5

Synthesis of some organosilicon ...

S/020/62/143/004/016/027
B106/B138

A. M. Kinnear, E. A. Perren, J. Chem. Soc., 1952, 3437.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: December 11, 1961

Table 1. Legend: (1) Compound; (2) boiling temperature, °C (mm); (3) found, %; (4) calculated, %; (5) yield, %; * n_D^{25} , or d_4^{25} , respectively; ** published data: n_D^{25} 1.4216; d_4^{25} 1.031.

Card 4/5

42515

S/O20/62/147/001/017/022
B106/B101

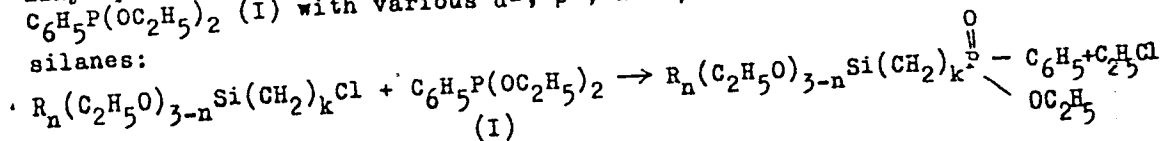
5,3650

AUTHORS: Chernyshev, Ye. A., Bugerenko, Ye. F., Nikolayeva, N. A.,
~~Petrov, A. D., Corresponding Member AS USSR~~

TITLE: Reaction between the diethyl ester of phenyl phosphinic acid
and α -, β -, and γ -chloro-alkyl alkyl alkoxy silanes

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 147, no. 1, 1962, 117-118

TEXT: In continuation of a study on the synthesis of compounds containing phosphorus and silicon (Ye. A. Chernyshev, Ye. F. Bugerenko et al., Izv. AN SSSR, OKhN, 1962, no. 6), ethyl esters of alkyl-ethoxy-silyl-substituted alkyl phenyl phosphinic acids were produced by reaction between $C_6H_5P(OC_2H_5)_2$ (I) with various α -, β -, and γ -chloro-alkyl alkyl alkoxy silanes:



n = 0, 1, 2, 3; k = 1, 2, 3; R = CH₃, C₂H₅, C₆H₅, CH₂=CHCH₂.

Card 1/3

S/O20/62/147/001/017/022
B106/B101

Reaction between the diethyl ...

These reactions are faster and more complete than the corresponding reactions between triethyl phosphite and alkyl halide alkyl alkoxy silanes. Substitution of one ethoxy group on the silicon atom of $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$ for one methyl group considerably shortens the time of reaction with I. The reaction of I with $\text{C}_2\text{H}_5\text{O}(\text{CH}_3)_2\text{SiCH}_2\text{Cl}$ is practically completed after 45 minutes, whereas the reaction of $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_2\text{Cl}$ with I is very vigorous and takes less than 10 minutes. In all reactions the molar ratio between I and chloro-alkyl alkyl alkoxy silane was 2 : 1, except in the case of $\text{CH}_2=\text{CHCH}_2(\text{CH}_3)_2\text{SiCH}_2\text{Cl}$ where it was 1 : 1. The reaction temperature was 109-240°C, the reaction time 10-45 minutes. The only exceptions were the reactions of I with $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$ on the one hand (600 minutes), and with $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_2\text{CH}_2\text{Cl}$ on the other (180 minutes). The yields were between 56.1% (reaction with $\text{CH}_2=\text{CHCH}_2(\text{CH}_3)_2\text{SiCH}_2\text{Cl}$) and 92.4% (reaction with $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiCH}_2\text{Cl}$). The reaction with $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_2\text{CH}_2\text{Cl}$ gave a 38.4% yield. Table 2 gives the physical data of the synthesized compounds.

Card 2/3

104-188 (3)

1.4890

1,0534

CHERNYSHEV, YE.A.

"Eine neue methode zur darstellung si-organischer verbindungen mit
aromatischen substituenten."

Report submitted to the 2nd Dresden Symp. on Organic and Non-Silicate
Silicon Chemistry.
Dresden, East Germany 26-30 March 1963

S/062/63/000/003/016/018
B101/B186

AUTHORS: Yegorov, Yu. P., Kirey, G. G., Samoylenko, S. A.,
Chernyshev, Ye. A., and Tolstikova, N. G.

TITLE: Infrared spectra of unsaturated organosilicon compounds con-
taining a pentamethyl disilyl group

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 3, 1963, 569 - 571

TEXT: The infrared spectra of the compounds $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2(\text{CH}_2)_n\text{C}=\text{CH}_2$,
 $n=0, 1, 2$, were investigated and the intensity and position of the $\nu(\text{C}=\text{C})$
bands were compared with one another. It was found that $\nu(\text{C}=\text{C})$ is
 1596 cm^{-1} with the vinyl derivative ($n = 0$) and that it is shifted to
 1635 cm^{-1} with the allyl derivative ($n = 1$); further, that it has maximal
intensity with this compound and that it is 1638 cm^{-1} with the γ -butyl
derivative ($n = 2$). The position of the other bands, as $\nu(\text{O-H})$, $\rho(\text{CH}_2)$
 $\rho(\text{CH})$ differs little from what is usual with alkenyl silanes. According-
Card 1/2

Infrared spectra of ...

S/062/63/000/003/016/018
B101/B186

ly substitution of the CH_3 group in the trisilyl group of an alkenyl silane by a $(\text{CH}_3)_3\text{Si}$ group does not entail any qualitative change of the spectrum. There are 1 figure and 1 table.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: October 29, 1962

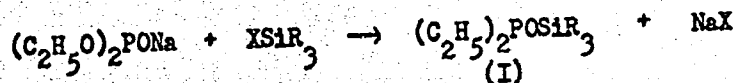
Card 2/2

CHERNYSHEV, Ye.A.; TOLSTIKOVA, N.G.; IVASHENKO, A.A.; ZELENETSKAYA, A.A.;
LEYTES, L.A.

Structure of the pentamethyldisilyl group in organosilicon compounds.
AN SSSR. Otd.khim. nauk no.4:664-666 Ap '63. (MIRA 16:3)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Silyl group) (Silicon organic compounds)

L 17068-63 EWP(j)/EPF(c)/EWT(m)/BDS S/062/63/000/004/020/022
 ASD Pc-4/Pr-4 RM/WW
 AUTHOR: Chernyshev, Ye. A. and Bugarenko, Ye. F.
 TITLE: On the structure of the products resulting from the reaction
 between trialkylhalosilanes and sodium diethylphosphite
 PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk,
 no. 4, 1963, 769-770
 TEXT: It was found that upon reacting trialkylhalosilanes with sodium
 diethylphosphite, their isomeric derivatives of trivalent phosphorus having
 the Si-O-P group are formed instead of the pentavalent phosphorus derivatives
 as proposed by Keeber and Post and by Newland:



where X=Cl, Br; R= alkyl group.
 The structure (I) like derivatives of trivalent phosphorus maintain its capability

Card 1/2

L 17068-63

On the structure of the

S/062/63/000/004/020/1122

to easily add sulfur and halides, and to enter into the Arbusov rearrangement with alkyl halides.

ASSOCIATION: Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N.D. Zelinskiy, Academy of Sciences USSR)

SUBMITTED: January 22, 1963

Card 2/2

S/190/63/005/003/010/024
B101/B186AUTHORS: Polyakova, A. M., Sakharova, A. A., Chernyshev, Ye. A.,
Krasnova, T. L., Korshak, V. V., Petrov, A. D.TITLE: Investigation into the polymerization of organometallic
styrene derivatives

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 3, 1963, 351-356

TEXT: Polymerization was made of $p\text{-R}_3\text{M}^{\text{IV}}\text{C}_6\text{H}_4\text{CH=CH}_2$, where $\text{R} = \text{CH}_3$ or C_2H_5 ,
 $\text{M}^{\text{IV}} = \text{Si, Sn or Ge}$ with or without pressure at 80°C in the presence of azo-
isobutyric dinitrile. Results:

monomer	pressure atm	time hr	yield %	$[\eta]$ 100 ml/g
$(\text{CH}_3)_3\text{SnC}_6\text{H}_4\text{CH=CH}_2$	6000	6	72	5.15
ditto	1	10	68	0.97
$(\text{C}_2\text{H}_5)_3\text{SnC}_6\text{H}_4\text{CH=CH}_2$	6000	6	60	2.10
ditto	1	10	53	0.23
$(\text{C}_2\text{H}_5)_3\text{GeC}_6\text{H}_4\text{CH=CH}_2$	6000	6	~100	insoluble
ditto	1	10	77	0.74
$(\text{C}_2\text{H}_5)_3\text{SiC}_6\text{H}_4\text{CH=CH}_2$	6000	6	~100	insoluble
ditto	1	10	82	0.54

Card 1/2

S/190/63/005/003/010/024
B101/B186

Investigation into the polymerization...

The thermomechanical curves of all polymers synthesized without pressure are similar. The zinc-containing polymer synthesized under pressure differed from the other Si and Ge polymers, also synthesized under pressure, by a step in the thermomechanical curve between 150 and 300°C. p-triethylstannyl- α -methylstyrene polymerized under pressure behaves in the same way. This is due to the C-Sn bond which, compared with C-Si and C-Ge, is less stable. X-ray analysis showed that the silyl and germyl compounds have amorphous structure, the stannyl compound, however, has had a quasi-crystalline structure. The IR spectra of all compounds have no absorption bands of the vinyl group so that polymerization is due to the rupture of the C-C bond of the vinyl group. In crude state, all polymers are transparent, glassy substances or viscous masses, after reprecipitation from benzene or xylene they are colorless fibrous substances. There are 1 figure and 1 table.

ASSOCIATION: Institut elementoorganicheskikh soedineniy AN SSSR (Institute of Elemental Organic Compounds AS USSR); Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy ASUSSR)

SUBMITTED: August 9, 1961
Card 2/2

CHERNYSHEV, Ye.A.; TOLSTIKOVA, N.G.

Synthesis of 1,1-dichloro-1-silaacenaphthene. Izv. AN SSSR.
Otd.khim.nauk no.6:1146 Je '63. (MIRA 16:7)

1. Institut organicheskoy khimii imeni Zelinskogo AN SSSR.
(Acenaphthene) (Silicon organic compounds)

S/020/63/148/004/021/025
B144/B101

AUTHORS: Chernyshev, Ye. A., Bugerenko, Ye. F., Petrov, A.D.,
Corresponding Member AS USSR

TITLE: Synthesis of some triethyl-silyl substituted alkyl-phosphinic
acids and their esters

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 148, no. 4, 1963,
875-877

TEXT: Esters having the general formula $(C_2H_5)_3Si(CH_2)_nPO(OC_2H_5)_2$ were synthesized, those with $n = 1$ or 3 according to the method by A.R. Gilbert (US pat. 2768193 (1956); Chem. Abstr., 51, 5816, (1957)) and those with $n = 0$ or 2 by the method of R.G. Linville (US pat. 2843615 (1958); Chem. Abstr., 53, 1147 (1959)). The compounds obtained, their boiling points, n_D^{20} , d_4^{20} and yields were: $(C_2H_5)_3SiCH_2PO(OC_2H_5)_2$ (I),

93-95°C/2.5 mm Hg, 1.4475, 0.9773, 46.7%; $(C_2H_5)_3Si(CH_2)_3PO(OC_2H_5)_2$ (III),
118-120°C/1.5 mm Hg, 1.4498, 0.9640, 43%; $(C_2H_5)_3Si(CH_2)_2PO(OC_2H_5)_2$ (II),

Card 1/3

S/020/63/148/004/021/025
B144/B101

Synthesis of some triethyl-silyl ...

116-118°C/2 mm Hg, 1.4493, 0.9726 (values cited from previous paper (DAN, 143, no. 4, 840, 1962)); $(C_2H_5)_3Si(CH_2)_4PO(OC_2H_5)_2$ (IV), 142-143°C/2 mm Hg, 1.4489, 0.9722, 63%. These esters were hydrolyzed with 38% HCl by heating for 24 hrs and yielded 96 - 98% acids. About 0.001 N solutions of these acids in 50% ethanol were titrated potentiometrically with 0.1 N NaOH at 20°C to determine the relation between their ionization constants and the position of their triethyl-siloxy group with respect to the P atom. The difference in the pK_1 of the

substituted and unsubstituted acids was 0.65 in the case of I and up to 0.15 for II, III, and IV. It is attributed to the induction effect of the $(C_2H_5)_3Si$ group, which is almost zero on substitution at the γ or δ C atoms of the alkyl chain. Similar results had previously been obtained by G. H. Barnes and M. P. David (J.Org.Chem., 25, 1191 (1960)) for other acids containing Si and P. There are 2 tables.

ASSOCIATION:

Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N.D. Zelinskiy of the Academy of Sciences USSR)

Synthesis of some triethyl-silyl ...

S/020/63/148/004/021/025
B144/B101

SUBMITTED: November 2, 1962

Card 3/3

CHERNYSHEV, Ye.A.; TOLSTIKOVA, N.G.

Interaction of chlorosilicon hydrides with thiophene and its chloro derivatives in the gas phase. *Izv.AN SSSR.Ser.khim.* no.9:1700-1703 S '64. (MIRA 17:10)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.

L 22664-65 EPF(c)/EPR/EWI(j)/EWI(m)/I Pc-4/Pr-4/Ps-4 RPL RM/WB/MLK
ACCESSION NR: AT5002117 S/0000/64/000/000/0103/0108

AUTHOR: Chernyshev, Ye. A., Petrov, A. D. (Deceased), Krasnova, T. L. B11

TITLE: Methods of synthesizing silicon-, germanium-, and tin-containing styrenes and aliphatic styrenes

SOURCE: AN SSSR. Institut neftekhimicheskogo sinteza. Sintez i svoystva monomerov (The synthesis and properties of monomers). Moscow: Izd-vo Nauka, 1964, 193-197

TOPIC TAGS: silicon containing styrene, germanium containing styrene, tin containing styrene, heteroorganic styrene, alpha methyl styrene, styrylchlorosilane

ABSTRACT: Two methods have been developed for the preparation of styrylchlorosilanes - a new class of organosilicon monomers. One method involves the reaction of p-styrylmagnesium chloride with silicon tetrachloride in accordance with the Leebnick-Ramsden method [J. Org. Chem. 23, 365 (1958)]. The other method involves the reaction of the Grignard reagent to the fourfold-excess of silicon tetrachloride at a temperature of 100°C. Under these conditions, the styrylchlorosilane yield is 50%. The other method involves high-temperature condensation of trichlorosilane and organosiliconhydrides with

Card 1/2

L 22664-65

ACCESSION NR: AT5002117

7
p-chloro- and p-chloro- α -methyl-styrene. During treatment with aqueous hydrofluoric acid, the chlorosilylstyrene changes into fluorosilylstyrene, and when treated with ethyl alcohol - into ethoxysilylstyrenes. The monomers were polymerized under pressure without pressure (with an initiator) and during γ irradiation. The degree of polymerization decreased in the following order: Si > Ge > Sn; with respect to viscosity, the order was Ge > Si > Sn. Infrared absorption spectra show that polymerization takes place through opening of the double bond with retention of the structure of the monomer unit. "The study was done with the participation of A.M. Polyakova, T.D. Nagibina, V.V. Korsakov, A. Sakharova, Ye. V. Volkova and A.I. Skokhin." The art. has: 4 tables and 10 figures.

ASSOCIATION: None

SUBMITTED: 30Jul64

ENCL: 00

SUB CODE: OC, GC

NO REF SOV: 009

OTHER: 008

Card 2/2

E 22666-65 EPF(c)/EPR/EWP(j)/EWT(m)/EWP(b)/T/EWP(t) pc-4/pr-4/ps-4 IJP(c)/
RPL RM/WY/JD/MLK
ACCESSION NR: AT5002120 S/0000/64/000/000/0123/0129

AUTHOR: Chernyshev, Ye. A.; Dolgays, M. Ye.

TITLE: Method of preparing aryfluorosilicon hydrides and their reactions

SOURCE: AN SSSR. Institut neftekhimicheskogo sinteza. Sintez i svoystva monomerov
(The synthesis and properties of monomers). Moscow. Izd-vo Nauka, 1964, 123-129

TOPIC TAGS: arylfluorosilicon hydride, silicon hydride, styrene addition, phenylchloro-
silane

ABSTRACT: A method has been developed for preparing arylfluorosilicon hydrides by re-
acting arylsilicon hydrides with aqueous hydrofluoric acid at temperatures of -40 to -60C.
In addition reactions with unsaturated compounds in the presence of H_2PtCl_6 , arylfluoro-
silicon hydrides are much more reactive than their chlorine-containing analogs. The aryl-
fluorosilyl group of the arylfluorosilicon hydrides adds to both atoms of the double bond of
styrene with the formation of predominantly α -isomer, whereas the phenylchlorosilyl group
of phenyldichlorosilane adds purely to the terminal carbon atom of the double bond. At
temperatures of 0 to 30C, the arylfluorosilicon hydrides react quantitatively with water,
alcohols, acids, and primary and secondary amines, with the replacement of hydrogen by

Card 1/2

L 22566-65

ACCESSION NR: AT5002120

hydroxyl, alkoxy-, acyloxy- or amino groups, respectively. Orig. art. has: 3 tables and 9 formulas.

ASSOCIATION: None

SUBMITTED: 30Jul64

ENCL: 00

SUB CODE: OC, GC

NO REF SOV: 007

OTHER: 007

Card 2/2

L 34137-65

ACCESSION NR: AT5006091

electron for various positions in the
discussion of the ESR spectra of anions of tin- and germanium-substituted
derivatives. The authors conclude that the experimental data accumulated thus far
are insufficient for a definitive solution of the problem of the distribution of
the unpaired electron in anions of tin and germanium derivatives of benzene. Orig.
art. has. 10 figures, 1 table and 2.

ASSOCIATION: Institut Khimicheskoy fiziki AN SSSR (Chemical physics institute,
AN SSSR)

Cont. 2-2

L 24837-65 EWT(m)/EFP(c)/EWP(j)/T Pc-L/Pr-L RM

ACCESSION NR: AP4047396

S/0062/64/000/010/1807/1814²⁰

AUTHOR: Cherny*shev, Ye. A.; Vangnits, Ye. V.; Gel'perina, V. M.;
Petrov, A. D. ¹⁹ B

TITLE: Synthesis of bis(organochlorosilyl)derivatives of aromatic hydrocarbons
and tris(trichlorosilyl)benzene

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 10, 1964, 1807-1814.

TOPIC TAGS: benzene, benzene derivative, synthesis, high temperature conden-
sation, disproportionation reaction, exchange reaction

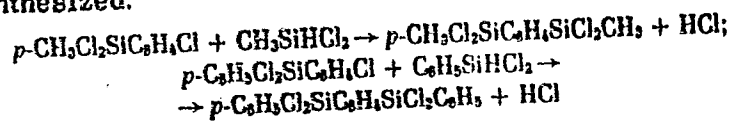
ABSTRACT: The high temperature condensation method described by Ye. A. Cherny*shev, V. F. Minorov and A. D. Petrov (Izv. AN SSSR. Otd. khim. n. 1960, 2147), wherein the reactants were contacted for about 30 seconds at about 580C, was utilized in the synthesis of a series of p-bis(organochlorosilyl)benzenes and of tris(trichlorosilyl)benzene. Disproportionation reactions did not occur in these gaseous reactions between the organochlorosilyl benzenes and chlorosilanes; only the silyl groups were exchanged. Hence pure bis(organodichlorosilyl)ben-

Card 1/3

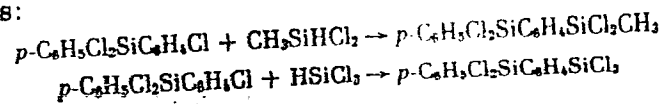
L 24857-65

ACCESSION NR: AP4047396

zenes were synthesized:



Gas phase condensation theoretically would not result in the synthesis of pure bis-silyl benzene derivatives having different methyldichlorosilyl and trichlorosilyl groups on one benzene ring. But compounds with different organochlorosilyl groups were separated by their differences in boiling temperatures, e. g. . in the following synthesis:



High temperature condensation of a four-fold excess of trichlorosilane with a mixture of dichlorophenyltrichlorosilane isomers gave a 13.5% yield of tris(trichlorosilyl)benzene which was methylated to tris(trimethylsilyl)benzene. The physical properties of the investigated compounds are tabulated. Orig. art. has: 1 table,

Card 2/3

L 24837-65

ACCESSION NR: AP4047396

1 figure and 10 equations

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii
nauk SSSR (Institute of Organic Chemistry, Academy of Sciences SSSR)

SUBMITTED: 21Jan63

ENCL: 00

SUB CODE: GC OC

NO REF SOV: 003 OTHER: 002

Card 3/3

L 24841-65 EWT(m)/EPF(c)/EWP(j)/T Pc-4/Pr-4 RM

ACCESSION NR: AP4047403

S/0062/64/000/010/1893/1895

AUTHOR: Cherny*shev, Ye. A.; Vangnits, Ye. V.; Petrov, A. D.

TITLE: Synthesis of bis(organochlorosilyl) derivatives of naphthalene

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 10, 1964, 1893-1895

TOPIC TAGS: naphthalene derivative, synthesis, organosilylnaphthalene, dichloronaphthalene

ABSTRACT: A non-catalytic gas phase condensation reaction was found usable for the synthesis of bis(organochlorosilyl) naphthalenes. Trichlorosilane or methyldichlorosilane were reacted with chloronaphthyltrichlorosilane, with dichloronaphthalene isomer mixtures and with 1, 4- and 1, 5-dichloronaphthalene. The high temperature condensations proceeded without isomerization at 575-580C in a quartz tube on 30 second contact time. The yields with methyldichlorosilane were somewhat lower than with trichlorosilane. The 1, 4- and 1, 5-dichloronaphthalenes were more reactive than p-dichlorobenzene. "The initial chloronaphthyl-

Card 1/2

L 24841-65

ACCESSION NR: AP4047403

trichlorosilanes, boiling 153-163C at (10 mm); n_D^{20} -1.6130 and dichloronaphthalene, boiling 106-120C (10 mm); melting at 50C, were supplied by G. V. Motsarev, whom we sincerely thank." Orig. art. has: 1 table and 1 equation

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry Academy of Sciences SSSR)

SUBMITTED: 02Mar64

ENCL: 00

SUB CODE: GC, OC

NO REF SOV: 001

OTHER: 003

Card 2/2

L 35512-65 EPP(c)/EWP(j)/EWT(m)/EWP(b)/T/EWP(t) Pc-4/Pr-4 IJP(c) RM/JD 8

ACCESSION NR: AP5008106

S/0062/65/000/002/0286/0291

AUTHOR: Bugerenko, Ye. F.; Chernyshev, Ye. A.; Petrov, A. D. (Deceased)

TITLE: Synthesis of compounds containing phosphorus and silicon

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 2, 1965, 286-291

TOPIC TAGS: phosphorus silicon compound, Arbuzov reaction, phosphite, diphenylphosphinite

ABSTRACT: As a continuation of the attempt to obtain a series of compounds containing both silicon and phosphorus, a number of α -, β -, and γ -haloalkylalkyl(alkoxy)silanes were condensed with triethyl phosphite and with the ethyl ester of diphenylphosphinous acid under the usual conditions of the Arbuzov reaction. Most products were obtained in good yield (60—90%); however, under the Arbuzov reaction conditions, β -chloroethyltriethoxysilane and γ , δ -dibromoethyltrimethylsilane tend to undergo β -cleavage. The yields and physical characteristics of the products are given in tabular form. It was found that compounds of the type $R_3SiCH_2PO(C_6H_5)_2$ undergo cleavage of the Si—C bond even on boiling with distilled water. Similar compounds without phenyl groups at the phosphorus atom are unaffected by

Card 1/2

L 35512-65

2

ACCESSION NR: AP5008106

concentrated hydrochloric acid. Under mild conditions, trimethylsilylmethyldiphenylphosphine adds oxygen, sulfur, and selenium to form the corresponding compounds of pentavalent phosphorus. Orig. art. has: 1 table. [VS]

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry, Academy of Sciences, SSSR)

SUBMITTED: 08Mar63

ENCL: 00

SUB CODE: OC,CC

NO REF SOV: 006

OTHER: 005

ATD PRESS: 1217

MB
Card 2/2

KARTSEV, G.N.; KOKOREVA, I.Yu.; SYRKIN, Ya.K.; MIRONOV, V.F.; CHERNYSHEV, Ye.A.

Dipole moments of organic compounds with a Si-Si bond. Zhur. strukt. khim.
6 no.2; 309-310 Mr-Apr '65. (MIRA 18:7)

1. Moskovskiy institut tonkoy khimicheskoy tekhnologii imeni Lomonosova.

L 32975-65 ENT(M)/EPF(c)/EPR/EMP(j) Doc. No. 10-1 12/11/75
ACCESSION NR: AP5007436 S/0286765/005/004/001.001

AUTHOR: Nagibina, T. D.; Yisenkova, L. S.; Alekberova, G. I.; Petrov, A. D.;
Chernyshev, Ye. A.; Krasnova, T. L.

TITLE: A method for producing synthetic rubber. Class 39, No. 168446

SOURCE: Byulleten' izobreteniy i tovarnykh znakov, no. 4, 1965, 62-63

TOPIC TAGS: synthetic rubber, emulsion polymerization

ABSTRACT: This Author's Certificate introduces a method for producing synthetic rubber by water emulsion copolymerization of divinyl with an unsaturated compound in the presence of an emulsifier and an initiator. The properties of the final product are improved by using *n*-trime... as the unsaturated...

ASSOCIATION: none

REMITTED: 25Sep62

ENTR: 100

SUB CODE: ME, 100

NO REF SOV: 000

OTHER: 000

Card 1/1

CHERNYSHEV, Ye.A.; DOLGAYA, M.Ye.; LUBUZH, Ye.D.

Addition of arylfluorosilicon hydrides to styrene. Izv. AN SSSR.
Ser. khim. no.4:650-654 '65. (MIRA 18:5)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.

BYKOVCHENKO, V.G.; ERMANSON, L.V.; CHERNYSHEV, Ye.A.

Kinetics of interaction of chlorosilicon hydrides with
chlorobenzene in the gas phase. Izv. AN SSSR. Ser. khim. no.11:
1949-1953 '65. (MIRA 18:11)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.

KULAYEVA, O.N.; CHERNYSHEV, Ye.A.; KAYUTENKO, L.A.; DOLGAYA, M.Ye.;
VOROB'YEVA, I.P.; POPOVA, E.A.; KLYACHKO, N.L.

Synthesis and test of the physiological activity of some compounds
of the kinin series. Fiziol. rast. 12 no.5:902-908 S-0 '65.
(MIRA 19:1)

1. Institut fiziologii rasteniy imeni Timiryazeva AN SSSR, Moskva
i Institut organicheskoy khimii imeni Zelinskogo AN SSSR, Moskva.

L 26359-66 EWT(m)/EPF(n)-2/SWP(j)/EWA(h)/EWA(l) WW/JW/GG/RM

ACC NR: AP6013381

SOURCE CODE: UR/0195/66/007/002/0230/0236

AUTHOR: Chkheidze, I. I.; Molin, Yu. N.; Mironov, V. F.; Chernyshev, Ye. A.; Buben, N. Ya.; Voyevodskiy, V. V.

ORG: Institute of Chemical Physics AN SSSR (Institut khimicheskoy fiziki AN SSSR); Institute of Kinetics and Combustion, SO AN SSSR (Institut kinetiki i goreniya SO AN SSSR); Institute of Organic Chemistry im. N. D. Zelinskiy, AN SSSR (Institut organicheskoy khimii AN SSSR)

TITLE: Formation of radicals during the radiolysis of organic solids. Part 3: EPR spectra and radiation yields of radicals in certain organosilicon compounds

SOURCE: Kinetika i kataliz, v. 7, no. 2, 1966, 230-236

TOPIC TAGS: free radical, organosilicon compound, irradiation effect, EPR spectrum

ABSTRACT: The EPR method was used to investigate the radical processes involved in the low-temperature radiolysis of certain organosilicon compounds with a view to determining the effect of the silicon atom entering into the aliphatic chain on the effectiveness and direction of primary radiochemical processes. The radiation yields of the radicals (G_R) formed by irradiating the compounds with fast electrons at temperatures from -130 to -180°C were determined by the EPR method. It was found that G_R for saturated and aromatic substituted derivatives of tetramethylsilane did not

UDC: 541.15-16

Card 1/2

L 26359-66

ACC NR: AP6013381

differ from G_R for hydrocarbons of similar structure and amounted to 4-5 1/100 ev and 0.2-0.6 1/100 ev, respectively. For compounds of the general formula $(CH_3)_3Si(CH_2)_nCH=CH_2$ ($n = 0, 1, 2$), the radiation yield is $G_R = 1$ 1/100 ev, which is approximately 4 times less than for hydrocarbons with double bond. Analysis of the EPR spectra showed that the introduction of a silicon atom in the aliphatic chain does not produce any appreciable changes in the radiolysis mechanism. Orig. art. has: 7 figures, 2 tables, 5 formulas.

SUB CODE: 07/20/ SUBM DATE: 12Sep64/ ORIG REF: 008/ OTH REF: 005

Card 2/2

ACC NR: AP6032591

SOURCE CODE: UR/0062/66/000/008/1391/1396

AUTHOR: Bugarenko, Ye. F.; Chernyshev, Ye. A.; Popov, Ye. M.

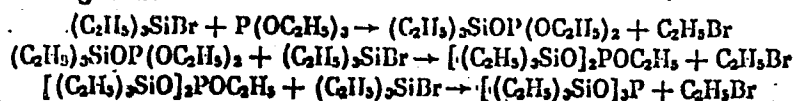
ORG: Institute of Organic Chemistry im. N. D. Zelinskiy, Academy of Sciences, SSSR
(Institut organicheskoy khimii Akademii nauk SSSR)

TITLE: Structure of products of reactions of triorganohalosilanes with sodium triethylphosphite and sodium dialkylphosphites

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 8, 1966, 1391-1396

TOPIC TAGS: silane, phosphite, sulfur compound, phosphorus compound, sodium compound

ABSTRACT: $(C_2H_5)_3SiBr$ and $P(OC_2H_5)_3$ were reacted at 155-180°C. The reaction is shown to have the following course:



i. e., to form derivatives of trivalent phosphorus containing the Si-O-P group. Similarly, the reactions

Card 1/2

UDC: 542.91+546.287+661.718.1

ACC NR: AP6036351

(A)

SOURCE CODE: UR/0138/66/000/011/0002/0002

AUTHOR: Nagibina, T. D.; Yassenkova, L. S.; Alikborova, G. I.; Petrov, A. D.;
Chornyshov, Ye. A.; Krasnova, T. L.

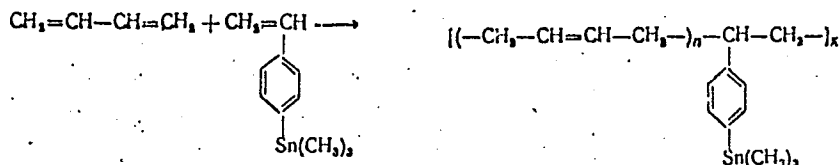
ORG: Institute of Organic Chemistry im. N. D. Zelinskiy, AN SSSR (Institut organi-
cheskoy khimii AN SSSR)

TITLE: Tin-containing synthetic rubber

SOURCE: Kauchuk i rezina, no. 11, 1966, 2

TOPIC TAGS: organotin compound, synthetic rubber, Copolymerization

ABSTRACT: A new type of tin-containing synthetic rubber (SKDOS-30) has been produced
by copolymerizing butadiene and p-trimethyltinstyrene at 60°C:



The yield of the copolymer was 60-70%. At the end of the reaction, the latex was
stabilized with a 2% alcohol solution of neozone D. The latex was coagulated with a

Card 1/2

UDC: (678.762.2+678.86).547.07.004.12