MIRONOV, V. F.

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Distr: 4E4j/4E2c(j)/4E3d

Some transformations of organosilicon compounds with functional groups in α- and γ-positions relative to the silicon atom. V. F. Mironov and N. A. Pogonkina (N. D. Zelinskii Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1957, 1199-205; cf. *C.A.* 51, 5505e.—The α-halide bond is more reactive than the γ-halide bond in reactions of halogen substituted silanes with nucleophilic reagents if the reaction is of bimol. nature (reaction with NaSCN). However since with KOAc the γ-position is more reactive, the mechanism of this replacement is evidently different. The γ-chlorides were prepd. by addn. of $RSiHCl_2$ to allyl or methallyl chlorides (Ponomarenko et al., *C.A.* 50, 13726e) as previously described but without N pressure: Pt-C is the best catalyst for the addn., as Pd-C or Raney Ni gave only $RSiCl_3$. $HSiCl_3$ does not add to allyl chloride in the presence of 2% Pt-C. $ClCH_2CHMeCH_2SiCl_2Me$ and MeMgCl gave 78% $ClCH_2CHMeCH_2SiMe_3$ (I), b_{14} 50-8°, n_D^{20} 1.4380, d_{20} 0.8812; similarly EtMgBr gave 80% $ClCH_2CHMeCH_2SiEt_2Me$, b_7 64-6°, 1.4531, 0.9003; however PrMgBr gave 48.7% $(ClCH_2CHMeCH_2SiPrMe)_2O$, b_3 150°, 1.4612, 0.9762. $ClCH_2CH_2CH_2SiEtCl_2$ and MeMgCl gave 70.5% $ClCH_2CH_2CH_2SiEtMe_2$, b[illegible] 55-7°, 1.4420, 0.8881. I refluxed 84 hrs. with NaSCN in EtOH gave 82.5% $Me_3SiCH_2CHMeCH_2SCN$, b_{16} 100-1°, 1.4710, 0.9239. Similarly was formed: 78.7% $Et_2MeSiCH_2CH_2CH_2SCN$, $b_{1.5}$ 85-6°, 1.4780, 0.9331, in 63 hrs.; 75% $PrMe_2SiCH_2CH_2CH_2SCN$, b_3 116-18°, 1.4709, 0.9161, in 62 hrs.; 85.3% $Et_2MeSiCH_2CHMeCH_2SCN$, $b_{1.5}$ 82-7°, 1.4801, 0.9320, in 83 hrs. NaSCN treated with Me_3SiCH_2Cl and $Me_3SiCH_2CH_2CH_2Cl$ in EtOH and refluxed 16.5 hrs. gave 13 g. unreacted γ-chloride and 73.6% Me_3SiCH_2SCN, b_3 46°, 1.4650, —, with but a little $Me_3SiCH_2CH_2CH_2SCN$, b_3 70°, 1.4690, — (13.5%). Heating Me_3SiCH_2Cl and $Me_3SiCH_2CH_2CH_2Cl$ with AcOK in AcOH in an autoclave at 200° 9 hrs. gave unreacted chlorides, 83.4% Me_3SiCH_2OAc, and

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V. F. Mironov + N. A. Pogonkina

48% $Me_3SiCH_2CH_2CH_2OAc$, b$_{760}$ 182.5°, 1.4218, 0.8743. Similarly was prepd. 84.5% $Me_3SiCH_2CHMeCH_2OAc$, b$_{12}$ 70-5°, 1.4230, 0.8710. Refluxing $Me_3Si(CH_2)_3Cl$ and EtONa-EtOH 30 hrs. gave 71% $Me_3Si(CH_2)_3OEt$, b. 155-6°, 1.4141, 0.7911; a 72.5% yield was obtained by heating in an autoclave 10 hrs. at 160° the above chloride with KOH in EtOH. This latter procedure at 200° gave 48.2% $Me_3SiCH_2CHMeCH_2OMe$, b$_{760}$ 160.5°, 1.4178, 0.7972. Mixed $Me_3SiCHClMe$ and $Me_3Si(CH_2)_2Cl$ gave 49% $Me_3SiCH:CH_2$, b. 54.5°, n_D^{20} 1.2852, and 60% $Me_3Si(CH_2)_2OMe$, b$_{760}$ 140°, 1.4102, 0.7898. Passage of $Me_3Si(CH_2)_3OAc$ through a glass tube at 500° gave 75.6% pure $Me_3SiCH_2CH:CH_2$, b. 84-6°, 1.4072, 0.7201. Similar pyrolysis of $MeSiCl_2CH_2CHMeCH_2Cl$ gave $MeSiCl_3$, unchanged chloride, and 51% chlorides, b. 145-50°, which with MeMgCl gave 40.7% mixed $Me_3SiCH_2CMe:CH_2$, $Me_3SiCH:CMe_2$, and $Me_3SiCH_2CH:CHMe$, b$_{760}$ 112-12.2°. Heating in an autoclave 5 hrs. at 160° $Me_3SiCH_2CH_2CH_2Cl$ with Et_2NH gave 58.7% $Me_3Si(CH_2)_3NEt_2$, b$_{760}$ 192.5°, 1.4308, 0.7836; ethiodide, m. 126-7°. $Me_3SiCH_2CHMeCH_2OAc$ kept 5 days in MeOH with a little H_2SO_4 gave 70.5% $Me_3SiCH_2CHMeCH_2OH$, b$_{12}$ 73.5°, 1.4334, 0.8331, which treated with a little MeONa and $CH_2:CHCN$ gave in 1 day 79.5% $Me_3SiCH_2CHMeCH_2OCH_2CH_2CN$, b$_{1.5}$ 97°, 1.4380, 0.8770. Me_3SiCH_2SCN kept in concd. H_2SO_4 1 day at 0° and 1 day at room temp. gave on aq. treatment a yellowish solid, m. 130° (decompn.), which appeared to be $Me_3SiCH_2SCONH_2$. $MeSiCl_2CH_2CHMe_2$, b$_{760}$ 137.8°, 1.4325, 1.0281. G. M. Kosolapoff

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Mironov, V.F.

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L 9758* (Russian.) Regularities in Chlorination of Silicoorganic Compounds. (O nekotorykh zakonomernostiakh khlorirovaniia kremneorganicheskikh soedinenii. V. F. Mironov and V. A. Ponomarenko. *Izvestiia Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, no. 2, Feb. 1957, p. 199-206.

From many examples, a general method of photochemical chlorination of alkyl silane and disilane chlorides was evolved, resulting in a high yield of monochlorinated products. The chlorinator is a simple apparatus where the monochloride formed is continuously separated from the zone of reaction and no longer has contact with chlorine. Advantages of this method over chlorination by SO_2Cl_2 include high yield and purity of the product.

PM

MIRONOV, V.F.; PETROV, A.D.

Synthesis and polymerization of compounds containing hydrogen and an unsaturated radical at the silicon atom. Izv.AN SSSR. Otd.khim.nauk no.3:383-384 Mr '57. (MLRA 10:5)

1.Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR.

(Polymerization) (Silicon organic compounds)

MIRONOV, V. F.

PETROV, A.D.; MIRONOV, V.F.; GLUKHOVTSEV, V.G.; YEGOROV, Yu.P.

Synthesis and properties of some of the bis-(trimethylsilil) propylenes. Izv. AN SSSR. Otd. khim. nauk no.9:1091-1100 S '57. (MIRA 10:12)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR. (Propene)

AUTHORS: Petrov, A. D., Mironov, V. F., 62-11-17/29
Komanicn, D.

TITLE: Synthesis of ß-Chloro and ß, ß-Dichlorovinylalkyldichlorosilanes (Sintez ß-Khlor- i ß, ß-dikhlorvinilalkildikhlorsilanov).

PERIODICAL: Izvestiya AN SSSR, Otdelenie Khimicheskikh Nauk, 1957, Nr 11, pp. 1393-1395 (USSR)

ABSTRACT: Here the best conditions for a synthesis of $ClCH = CHSiCl_3$, as well as the alkyl- and alkoxy-derivatives of them, among them also the difunctional (in the silicon atom) ß-chlorovinylethylenedichlorosilane, were obtained. The development of C. L. Agre's (reference 2) was continued here and it was ascertained that the trichloroethylene can also be condensed with the alkyldichlorosilanes. This is a very simple way for the synthesis of the dichlorodialkylsilanes with the functional groups in the alkyl-chain

$$Cl_2C = CHCl + HSiRCl_2 \rightarrow Cl_2C = CHSiCl_2R + HCl$$

Card 1/2 where $R = CH_3$ and C_2H_5. It can be judged on the course of

Synthesis of β-Chloro and β, β-Dichlorovinylalkyldichlorosilanes. 62-11-17/29

the reaction according to the given equation and on the position of the chlorineatoms according to the corresponding physical properties of the β,β-dichlorovinyltriethylsilane which were obtained by Agre and by the authors. There are 1 table, and 3 references, 1 of which is Slavic.

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

SUBMITTED: June 21, 1957.

AVAILABLE: Library of Congress

Card 2/2

AUTHORS: Petrov, A.D., Mironov, V.F.

TITLE: Magnesium-Organic Synthesis of the Vinyl Derivatives of Silicon, Germanium, and Tin (Magniyorganicheskiy sintez vinil'nykh proizvodnykh kremniya, germaniya i olova)

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1957, Nr 12, pp. 1491-1493 (USSR)

ABSTRACT: The first compound of this group $(C_2H_5)_3 SiCH = CH_2$ was obtained by means of the chlorination of tetraethylsilane up to $CH_3 Cl CHSi(C_2H_5)_3$ and by its dehydrochlorination by alcoholic alkalinity. This synthesis was later also used for other silicon-organic compounds (especially for $C_2H_5SiCl_3$) in which case other dehydrochlorinating reagents were employed. In the same manner the authors found the synthesis of vinyltrichlorogermanium. An excellent method of synthesis of the Grignard (Grin'yar) reagent gave rise to the investigation of the possibility of the condensation of this reagent with chloroalkylsilanes and stannanes. It was shown that the condensation of the reagent according to Normant ($CH_2 = CHMgBr$) with chloroalkylsilanes [illegible] permits the synthesis with high yields of vinyl derivatives of the aforementioned elements, with any number

Card 1/2

Magnesium-Organic Synthesis of the Vinyl Derivatives
of Silicon, Germanium, and Tin [illegible]

of vinyl radicals. There are [illegible] references, [illegible] of which are Slavic.

ASSOCIATION: Institute for Organic Chemistry AS USSR imeni N.D.Zelinskiy
(Institut organicheskoy khimii im. N.D.Zelinskogo Akademii nauk
SSSR).

SUBMITTED: July 5, 1957

AVAILABLE: Library of Congress

Card 2/2
1. Tetraethyl-silane-Chlorination 2. Tetraethyl-sylane-Dechlorination
3. Vinyltrichlorgermanium-Synthesis

MIRONOV, V. F.

11328* (Russian.) Synthesis and Properties of Silicon Hydrocarbons and Their Derivatives. Sintez i svoistva kremneuglevodorodov i ikh proizvodnykh. A. D. Petrov, V. F. Mironov, and E. A. Chernyshev. *Uspekhi Khimii*, v. 26, ~~Mar. 1957,~~ p. 292-344.

Direct synthesis of silico-organic compounds. Halogenation and dehydrohalogenation of the compounds; Friedel-Craft reactions. Silicon hydrocarbons of aliphatic aromatic, fatty-aromatic, and the naphthene series. Polymerization and copolymerization of alkenylsilanes.

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MIRONOV, V.F.

Distr: 4E4j/4E2c(j)/4E3d

Synthesis of α-trimethylsilylstyrene, 1-trimethylsilylcyclohexene, and other unsaturated organosilicon compounds. A. D. Petrov, V. F. Mironov, and V. G. Glukhovtsev (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* 27, 1535-9(1957); cf. *C.A.* 50, 16663f.—To 23 g. Na in finely divided state under Et_2O there was added [illegible] g. Me_3SiCl, 5 ml. 1-chlorocyclohexene, and 2 ml. EtOAc; after a reaction had commenced, 60 g. 1-chlorocyclohexene was added over 2 hrs. yielding 50 g. *1-trimethylsilylcyclohexene*, b_{760} 171.5°, n_D^{20} 1.4628, d_{20} 0.8351. Raman spectrum (cm.$^{-1}$): 215(4), 256(1), 298(2), 321(0), 355(2), 381(0), 402(6), 439(1), 491(1), 539(3), 632(5), 660(0), 694(3), 729(0), 753-(1), 837(3), 855(2), 911(2), 943(1), 970(1), 1000(1), 1039(2), 1079(2), 1124(0), 1179(2), 1196(1), 1251(1), 1271(3), 1308-(2), 1354(2), 1377(1), 1409(1), 1425(4), 1448(1), 1460(1), 1620(4), 1575(0), 1563(0), 2833(4), 2865(8), 2900(10), 2933-(2), 2957(9), 3005(2), 3032(1). Similarly, to 23 g. powd. Na in Et_2O was added 60 g. Me_3SiCl followed over 40 min. by 69 g. $PhCCl{:}CH_2$; after 2 days there was obtained 32 g. $Me_3SiCPh{:}CH_2$, b_5 52°, 1.5115, 0.8866. To $PhCH{:}CHMgBr$ from 6.3 g. Mg and 57 g. $PhCH{:}CHBr$ was added 30 g. $PrMe_2SiCl$; after distn. of the Et_2O the residue was heated on a steam bath 6 hrs. then treated with H_2O to yield 12 g. $PrMe_2SiCH{:}CHPh$, b_{25} 133°, 1.5218, 0.8908. To 250 g. abs. MeOH, 70 g. pyridine, and 250 ml. C_6H_6 was slowly added 33 g. $({:}CHSiCl_3)_2$ to yield after 2 days 22.5 g. $[{:}CHSi(OMe)_3]_2$.

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A. D. Petrov, V. F. Mironov etc.

b 80°, b 228-9°, 1.4185, 1.0721. Similar reaction of CH_2:-
CClSiCl$_3$ gave 60% CH_2:CClSi(OMe)$_3$, b 157.4°, 1.4183,
1.1109. Use of EtOH similarly gave CH_2:CClSi(OEt)$_3$,
b 184° (some decompn.), 1.4161, 1.0145. Similarly, Cl-
CH:CHSiCl$_3$ gave 41% (MeO)$_3$SiCH:CHCl, b 164°,
1.4195, 1.1097. Similarly, EtMe$_2$SiCl and 1-chloro-2-butyn-
4-ol gave Me$_2$EtSiOCH$_2$C:CCH$_2$Cl, b$_8$ 58°, 1.4593, 0.9965;
similarly was prepd. 45% Me$_3$SiOCH$_2$C:CCH$_2$Cl, b$_8$ 71°,
1.4538, 0.9988. To 40 g. powd. Na in MePh was added 8
ml. EtOAc followed by 78.5 g. Et$_2$SiCl$_2$ at 50°; after re-
fluxing 2 hrs. and standing overnight the mixt. yielded a
range of products with mol. wts. up to 1200 and b$_1$ above
240°. Reaction of 10 g. Me$_3$SiCH$_2$CH:CH$_2$ and 48 g. Me-
COSH overnight gave 14.5 g. Me$_3$SiCH$_2$CHMeSCOMe, b
123-7°, 1.4652, 0.9198. An equimolar mixt. of (MeO)$_2$PS$_2$H
and MePhSi(CH$_2$CH:CH$_2$)$_2$ gave 90% MePhSi[CH$_2$CHMe-
SP(S)(OMe)$_2$]$_2$, n_D^{20} 1.5550, d_{20} 1.1700. Me$_2$SiCl$_2$ (450 g.)
and BuMgBr from 500 g. BuBr gave 47.5% BuMe$_2$SiCl,
b 138.4°, 1.4205, 0.8751. Similarly were prepd. 37.5%
PrMe$_2$SiCl, b 115.8°, 1.4138, 0.8726, and PrEt$_2$SiCl,
21.2%, b 166.4°, 1.4347, 1.9024. To BuMgBr from 262 g.
BuBr was added 65 g. CH_2:CHSiCl$_3$ and after 5 hrs. re-
fluxing the mixt. was treated with H_2O yielding 78.9% Bu$_3$-
SiCH:CH$_2$, b 128°, b 123°, 1.4494, 0.7938. Similarly
were obtained 65% Me$_3$SiCH:CH$_2$, b 54.6°, 1.3910,
0.6903; 67% Et$_3$SiCH:CH$_2$, b 146.5°, 1.4345, 0.7728;
51.5% Pr$_3$SiCH:CH$_2$, b 198.2°, 1.4430, 0.7853.

G. M. Kosolapoff

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Mironov, V.F.

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Polymerization of unsaturated organosilicon compounds under pressure. IV. Mono- and disilanes. V. V. Korshak, A. M. Polyakova, A. A. Sakharova, A. D. Petrov, V. F. Mironov, V. G. Glukhovtsev, and G. I. Nikishin (Inst. Heterocycl. Compds., Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* 27, 2445-9(1957); cf. *C.A.* 49, 15727i; 50, 16705e; 51, 11988a.—It was shown that vinylsilanes which carry Et and MeO groups are more prone to polymeriz. than are their analogs with Me, Pr, and other radicals. The allyl derivs. are more readily polymerizable than are methallyl analogs. The monomers were heated under 6000 atm. pressure at 130° with up to 3% (Me$_3$CO)$_2$ initiator. Polymers were formed from: Me$_3$SiCH:CH$_2$, Et$_3$SiCH:CH$_2$, Pr$_3$SiCH:CH$_2$, Bu$_3$SiCH:CH$_2$, Et$_3$SiCH$_2$CH:CH$_2$, Me$_3$SiCMe:CHMe, Me$_3$SiCMe:CHCH$_2$OCH$_2$CH$_2$CN, Me$_3$SiCMe:CHCH$_2$OH, 1-C$_{10}$H$_7$Si(CH$_2$CH:CH$_2$)$_3$, 1-C$_{10}$H$_7$Si(OCH$_2$CH:CH$_2$)$_3$, [(MeO)$_3$SiCH:]$_2$, (MeO)$_3$SiCH:CHCl, (MeO)$_3$SiCCl:CH$_2$, Me$_3$SiCH$_2$C(:CH$_2$)CH$_2$Cl, CCl$_2$Si(CH$_2$CH:CH$_2$)$_2$, PrHSi(CH$_2$CMe:CH$_2$)$_2$, iso-PrHSi(CH$_2$CH:CH$_2$)$_2$, BuHSi(CH$_2$CH:CH$_2$)$_2$, iso-BuHSi(CH$_2$CH:CH$_2$)$_2$, (CH$_2$)$_4$Si(CH$_2$CH:CH$_2$)$_2$. Polymers were not formed from: EtMe$_2$SiCH:CMe$_2$, EtMe$_2$SiCH:CHMe, Me$_3$SiCMe:CHMe at 1 atm. pressure, Me$_3$SiCHMeCH:CHMe, Et$_3$SiCMe:CHCH$_2$OCH$_2$CH$_2$CN, PrMe$_2$SiCH:CHPh, Me$_3$SiC(:CH$_2$)Ph, Me$_2$Si$\overline{\text{C:CH.(C}}H_2$)$_3$, MeCH:C(SiMe$_3$)$_2$, Me$_3$SiCH:CMeSiMe$_3$, Me$_3$SiCH$_2$CH:CHCH$_2$SiMe$_3$, Et$_3$SiOCH$_2$CH:CMeSiEt$_3$, and CCl$_3$SiCH$_2$CH:CH$_2$ (sic). G. M. Kosolapoff

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Distr: 4E4j/4E3d/4E2c(j)

KORSHAK, V.V.; POLYAKOVA, A.M.; PETROV, A.D.; MIRONOV, V.F.

Polymerization of unsaturated germanium organic compounds. Dokl. AN SSSR 112 no.3:436-438 Ja '57. (MLRA 10:4)

1. Chlen-korrespondent AN SSSR (for Korshak, Petrov, Mironov)
2. Institut elementoorganicheskikh soyedineniy i Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR.
(Germanium organic compounds)
(Polymerization)

MIRONOV, V. (Moscow)

"Vergleich der Reaktionsbereitschaft von Elementen der IV. Gruppe des Periodensystems und Synthese von Einigen Verbindungen"

paper submitted for the Symposium on Organic and Non-Siliceous Silicon Chemistry, Dresden, 12-14 May 1958.

MIRONOV, V. F.

V. F. Mironov, V. A. Ponomarenko, G. Ya. Vzenkova, I. Ye. Dolgiy and A. D. Petrov, "The Synthesis of Germanium-organic Compounds."

Report presented at the Second All-union Conference on the Chemistry and Practical Application of Silicon-Organic Compounds held in Leningrad from 25-27 September 1958.
Zhurnal prikladnoy khimii, 1959, Nr 1, pp 235-240 (USSR)

AUTHORS: Yegorov, Yu. P., Leytes, L. A., Mironov, V. F., [illegible]

TITLE: Transconfiguration of 1,2-Disilylsubstituted Ethylenes (O trans-konfiguratsii 1,2-disililzameshchennykh etilenov)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 4, pp. 510-512 (USSR)

ABSTRACT: In previous papers (Refs 1-3) the authors described for the first time the synthesis of 1,2-bis-(trichlorosilyl)-ethylene and 1,2-bis-(trimethylsilyl)-ethylene as well as the combination dispersion of light in the latter compounds. They also uttered the assumption that the widening of the frequency of the binary binding to 20 cm^{-1} observed in this spectrum can possibly be explained by the cis-trans-isomerism. The KRS-spectrum (Ref 4) of 1,2-bis-(trichlorosilyl)-ethylene was described by Batuyev and others (spectrograph KPC-11). The authors of the present paper report that they found the IK-spectra of 1,2-bis-(trichlorosilyl)-ethylene and 1,2-bis-(trimethyl)-ethylene (within the range of from 700-1700 cm^{-1}).

Card 1/2

Transconfiguration of 1,2-Disilylsubstituted Ethylenes [illegible]

It was reported that these molecules have centrosymmetrical transconfiguration. There are 2 figures, 2 tables, and [illegible] references, 5 of which is Soviet.

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

SUBMITTED: November 27, 1957

AVAILABLE: Library of Congress

1. **Disilylsubstituted ethylenes—Transconfigurations**

Card 2/2

AUTHORS: Mironov, V.F., Petrov, A. D. 62-58-6-27/37

TITLE: The Synthesis of Vinyl-and β-Halogenvinyl-Substituted Silanes (Sintez vinil- i β-galogenvinilzameshchennykh silanov)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 6, pp. 787 - 788 (USSR)

ABSTRACT: In the present paper the authors tell of the successfully carried out condensation of CH_3Cl_2SiH with chlorovinyl during the common passage through an empty tube heated up to 550°:

$$CH_3Cl_2SiH + ClCH=CH_2 \xrightarrow{550^{\circ}} CH_3Cl_2SiCH=CH_2+HCl.$$

The yield of vinylmethyldichlorosilane in this reaction amounts to 50%. In the dehydrobromination of $Cl_3SiCHBrCH_2Br$ quinoline splits off the bromine-β-atom, whereas aluminium chloride splits off the bromine-α-atom. α- and β- bromovinyltrimethylsilanes form reactive Grignard reagents in tetrahydrofuran. There are 5 references, 3 of which are Soviet.

Card 1/2

The Synthesis of Vinyl- and β-Halogenvinyl- -Substituted Silanes 62-58-6-23/37

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

SUBMITTED: January 28, 1958

1. Silanes--Synthesis 2. Substitution reactions 3. Vinyl chlorides--Chemical reactions

Card 2/2

SOV/[illegible]

AUTHORS: Petrov, A. D., Mironov, V. F., Ponomarenko, V. A., Sadykh-Zade, S. I., Chernyshev, Ye. A.

TITLE: Synthesis of New Types of Silicon Containing Monomers (Sintez novykh vidov kremneorganicheskikh monomerov)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 8, pp 954-963 (USSR)

ABSTRACT: This lecture was delivered at the General Meeting of the Department of Chemical Sciences of the AS USSR in April [illegible] 1958. First the previous paper (Ref [illegible]) and the papers written by other authors (Refs 2 and 3) are discussed in short. Then the lecture deals with the three subjects: a) The [illegible] binding of hydride silanes with unsaturated and aromatic compounds. b) The condensation of hydride silanes with alkyl-, aryl- and alkenyl halides at high temperature. c) The synthesis of polymerizing silicon hydrocarbons and their derivatives. The result of the experiments carried out is as follows: In the presence of H_2PtCl_6 alkyl [illegible] silanes bind with $CH\equiv CH$, $CH_2=CH_2$, $CH_2=CHCH_3$ (at temperatures of from [illegible]

Card 1/2

Sy[illegible] f New Typ[illegible] f S [illegible] Containing [illegible] SOV [illegible]

[illegible] kenyl [illegible] pheric [illegible]

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chem. imeni N. D. Ze[illegible], AS USSR)

SUBMITTED: May 4, 19[illegible]

Card 2/2

AUTHORS: Mironov, V. F., Nikishin, G. I.

TITLE: The Relation Between the [illegible] Compounds and Their Molecular Re[illegible] mezhdu strukturoy [illegible] i ikh molekulyarnymi re[illegible]

PERIODICAL: Izvestiya Akademii [illegible] SSSR. [illegible] 195[illegible], Nr 9, p. [illegible] (USSR)

ABSTRACT: The method of calculating [illegible] of [illegible] compounds has been based upon t[illegible] of the summation of the individual [illegible] each bond in the molecule. The [illegible] of the molecule must be taken into [illegible] calculation. The [illegible] of this [illegible] silicon compounds is only briefly [illegible] papers which [illegible] it (Re[illegible]). [illegible] this paper succeeded in [illegible] whose presence in [illegible] by an exaltation in the [illegible] several simil[illegible] in the [illegible]

Card 1/2

The Relation Between the Structure of Some Or[illegible]
Compounds and Their Molecular Refraction

newly-discovered radicals. It was found that [illegible] in the molecular refraction is an additive [illegible] which is directly proportional to the [illegible] which cause this increased refraction. T[illegible] ascertained the group refraction contrib[illegible] radicals which were bonded to the silicon atom. T[illegible] 5 tables and 38 references, 2[illegible] of which [illegible].

ASSOCIATION: Institut organicheskoy khimii im. N.D.Z[illegible] SSSR (Institute of Organic C[illegible]

SUBMITTED: February 15, 19[illegible]

Card 2/2

5(4), 15(6)

AUTHORS: Kartsev, G. N., Syrkin, Ya. K., Corresponding Member, Academy of Sciences, USSR, Mironov, V. F., Chernyshev, Ye.A. SOV/20-122-1-27/44

TITLE: The Dipole Moments of Some Silicon-Organic Compounds (Dipol'nyye momenty nekotorykh kremniyorganicheskikh soyedineniy)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 1, pp 99-102 (USSR)

ABSTRACT: The authors measured the dipole moments of some silicon-organic compounds according to the heterodyne method at 25° in benzene. The extrapolated polarizations were calculated according to a formula of Hedestrand. For compounds which contain silicon, the atomic polarization has to be taken into account. The experimental results are given in a table. A distinctive peculiarity of the silicon compounds is the increased polarity with respect to the corresponding carbon bonds. According to the available data, the bond moment of Si-H may be estimated to 1D, and the bond moment of Si-C - to 0,6D. In both of these cases, the positive end of the dipole is directed towards the silicon. In the bonds

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The Dipole Moments of Some Silicon-Organic Compounds SOV/20-122-1-27/44

Si-O and Si-halogen, the weight of the ionic state is higher. Numerous and detailed data are given. There are 1 table and 5 references.

ASSOCIATION: Moskovskiy Institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova
("Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov")

SUBMITTED: May 15, 1958

Card 2/2

5(3)

AUTHORS: Mironov, V. F., Pogonkina, N. A. [illegible]-1-14/38

TITLE: Addition of Thioacetic Acid to Alkenyl-Trialkyl Silanes and Synthesis of Mercaptans Containing Silicon (Prisoyedineniye tiouksusnoy kisloty k alkeniltrialkilsilanam i sintez kremneorganicheskikh merkaptanov)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, [illegible] (USSR)

ABSTRACT: In the present paper the authors found that thioacetic acid is added not only to dialkyl silanes, but also to other unsaturated silicon hydrides which possess the double bond in the α-, β- and γ-position. Various organo-silicon thioacetates were saponified with alkali in order to synthesize silicomercaptans. It was found that the silicon acetates obtained from vinyl-, allyl-, γ-butenyl and other alkenyl-trialkyl silanes are easily saponified up to silicomercaptans. They are cyanoethylated in high yield by akrylnitrile. The constants and infra-red spectra of products which were obtained by cyanoethylation according to the left and to the right of scheme 2, proved

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Addition of Thioacetic Acid to Alkenyl-Trialkyl Silanes [illegible]-14/38
and Synthesis of Mercaptans Containing Silicon

to be identical. With reference to the order of addition of $HSCOCH_3$ to γ-butenyl-trialkyl silanes it is assumed that the hydrolysis of the thioacetates obtained leads to the formation of δ-silicomercaptans. The authors failed to estimate the relative reactivity of the silicomercaptans of the homologous series $R_3Si(CH_2)_nSH$ (n = 1,2,3 and 4) in the reaction with akrylnitrile since all of them react rapidly and smoothly with akrylnitrile. The addition of ethyl mercaptan takes place in the same easy way. γ-(trimethyl-silyl)-propyl-ethyl sulfide was synthesized to prove its order of addition. The infrared spectra of this γ-silicon sulfide and the silicon sulfide obtained from $(CH_3)_3SiC_3H_5$ and ethyl mercaptan proved to be identical. However, the silicon sulfide obtained from trimethyl-allyl silane in the saponification of the adduct of dimethyl-dithiophosphoric acid was quite different. Thus, the assumption is confirmed (Ref 4) that the addition of dialkyl-dithiophosphoric acid to trialkyl-allyl silanes takes place according to Markovnikov's

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Addition of Thioacetic Acid to Alkenyl-Trialkyl Silanes [illegible]
and Synthesis of Mercaptans Containing Silicon

rule, like HBr. It was stated that an indivisible poly-sulfide mixture is easily produced by trialkyl-[illegible] silanes on heating with elementary sulfur. The table gives 27 organo-silicon compounds synthesized by the authors which so far have not been described in publications. There are 1 table and 7 references, [illegible] of which are Soviet.

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 10, 1957

Card 3/3

5(3)

AUTHORS: Korshak, V. V., Polyakova, A. M., [illegible]
Petrov, A. [illegible]

TITLE: Polymerization of Vinyl and Allyl Derivatives of El[illegible] of the IVth Group (Polimerizatsiya vinil[illegible] nykh elementov IV gruppy)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye [illegible] 195[illegible], Nr [illegible], pp 17[illegible] - 180 (USSR)

ABSTRACT: In the present communication the authors [illegible] the reactivity of unsaturated compounds of el[illegible] of the IVth group in ion reactions and radical polymerization. It was found that the reactivity of these compounds increases in ion reactions in the order C < Si < Ge < Sn. The inclination of the same compounds to radical polymerization increases in the inverse order of Sn < Ge < C < Si([illegible] [illegible]. Among the structurally similar elements of the IVth group [illegible] investigated alkyl silanes incline most readily to polymerization. Thus, no deactivating effect is [illegible] by the silicon atom in polymerization unlike in [illegible] carbon atoms in structurally similar olefins [illegible]

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Polymerization of Vinyl and Allyl Derivatives of El[illegible]
of the IVth Group

alkyl-allylstannanes do not polymerize [illegible] capable of forming polymers with methyl [illegible] Furthermore, copolymerization products of [illegible] germanium were obtained with styrene. There [illegible] tables, and 7 references, [illegible] of which are Sov[illegible]

ASSOCIATION: Institut elementoorganicheskikh soyedineniy (Institute of Elemental Organic Compounds) Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of [illegible] Chemistry imeni N. D. Zelinskiy of the [illegible] USSR)

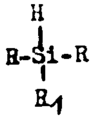
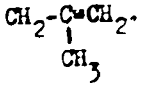
SUBMITTED: June 25, 1958

Card 2/2

5(3)
AUTHORS: Korshak, V. V., Polyakova, A. M., Mironov, V. F., SOV/62-59-6-27/36
Petrov, A. D., Tembovtseva, V. S.

TITLE: On the Polymerization Mechanism of the Alkenylhydride Silanes
(O mekhanizme polimerizatsii alkenilgidridsilanov)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 1116 - 1125 (USSR)

ABSTRACT: The polymerization capability of monoalkenylhydride silane with the general formula  $R-\overset{H}{\underset{R_1}{Si}}-R$ was investigated. In this formula $R = CH_3, C_2H_5, Cl, OC_2H_5; R_1 = CH_2-CH=CH_2, OCH_2-CH=CH_2$ and  $CH_2-\underset{CH_3}{C}=CH_2$.

The peroxide of the tertiary buthyl, and platinum on coal served as polymerizers. Like in the case of other investigations (Refs 2,3), polymers of the general formula $(CH_3)_3Si(CH_2)_nSi(CH_3)_3$ with n=1,2,3 (I) n=1 (II) n=2 (III) n=3 were found. The structure of the polymers obtained was determined by means of the infrared spectrum.

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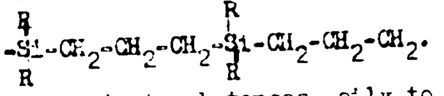
On the Polymerization Mechanism of the Alkenylhydride Silanes SOV/62-59-6-27/36

The spectra were compared with the spectrum of the polymer produced from $(CH_3)_2H.SiCH_2-CH=CH_2$ by heating with platinum on coal (IV). L. A. Leytes and V. N. Smorchkov plotted and interpreted the spectra. The investigations of the infrared spectra showed that the allyldialkyl (aryl) silanes polymerize in a different way under formation of differently structured polymers in dependence on the polymerizer. In the presence of the buthyl peroxide and at a pressure of 6000 atmospheres a macro molecule (A) was formed, in which the S-H bond is not split up. This conclusion is made because of the presence of the band (2100 cm^{-1}) characteristic of the S-H group, which is also to be found in the spectrum of the initial monomer and in the spectrum (IV). The other form of polymers (B) is produced in the presence of platinum on coal. They contain the band weakly mentioned either in a weak form or not at all, while the bands in the range of from 1050-1150 cm^{-1} are clearly determined. These polymers exhibit the following structure:



$-\underset{R}{\overset{R}{Si}}-CH_2-CH_2-CH_2-\underset{R}{\overset{R}{Si}}-CH_2-CH_2-CH_2$. The polymers obtained are differently consistent substances, oily to solid, in dependence on the

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On the Polymerization Mechanism of the Alkenylhydride Silanes SOV/62-59-6-27/36

character of the radicals on the silicon atom. The data concerning the different polymers are given in table 1. In the experimental part the syntheses of the single polymers from the monomers concerning are described. Table 3 gives the physical constants of the initial monomers and figures 1-16 show the infrared spectra of the different polymers. There are 16 figures, 2 tables, and 5 references, 4 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences, USSR) and 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: September 3, 1957

Card 3/3

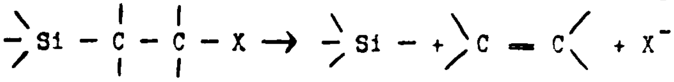
5(3)

AUTHORS: Mironov, V. F., Nepomnina, V. V. SOV/62-59-7-12/38

TITLE: The Influence of the Chlorosilyl Groups on the Mobility of the Chlorine Atom in β-Chloralkylsilanes During Their Dehydrochlorination by Quinoline (Vliyaniye khlorsilil'nykh grupp na podvizhnost' atoma khlora v β-khloralkilsilanakh pri degidrokhlorirovanii ikh khinolinom)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 7, pp 1231 - 1237 (USSR)

ABSTRACT: In the present paper a β-decomposition product is obtained by the dehydrochlorination of $CH_3Cl_2SiCH_2CH_2Cl$ with quinoline which is produced according to the following reaction scheme:



(X = halogen).

The reaction was more intensively investigated in a series of compounds of the type $Cl_nR_{3-n}SiCH_2CH_2Cl$. HCl is splitted off. It was observed that the formation of a β-product $Cl_nR_{3-n}SiCH=CH_2$ proceeds the more easily the greater n is. From the fur-

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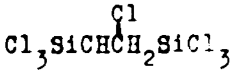
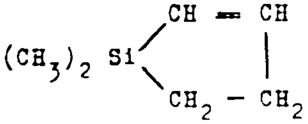
The Influence of the Chlorosilyl Groups on the Mobility of the Chlorine Atom in β-Chloralkylsilanes During Their Dehydrochlorination by Quinoline SOV/62-59-7-12/38

ther investigation of the mobility of the β-chlorine atom it follows that this atom is more mobile in the chlorine compounds



$Cl_3SiCH\overset{Cl}{C}H_2SiCl_3$ and in α,α-, α,β-, and β,β-dichloroethyl-trichlorosilane than in the β-monochloroalkyl-trichlorosilanes. Moreover, the following substance was obtained from the investigations:



1,1-dimethyl-cyclosilicon-pentene-2.

The different reactions and synthesis methods are described in detail in the experimental part. There are 18 references, [illegible] of which are Soviet.

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The Influence of the Chlorosilyl Groups on the Mobility of the Chlorine Atom in β-Chloralkylsilanes During Their Dehydrochlorination by Quinoline

SOV/62-59-7-12/38

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: November 23, 1957

Card 3/3

5(4)

AUTHORS: Mironov, V. F., Yegorov, Yu. P., Petrov, A. D. SOV/62-59-8-10/42

TITLE: Relative Reactivities of Some Organic Silicon, Germanium, and Tin Compounds and Their Raman Spectra

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 8, pp 1400-1407 (USSR)

ABSTRACT: In continuation of previous papers (Refs 1-3) the present paper deals with the addition reactions of compounds of the type $R_2MCH=CH_2$ as a function of the nature of the central atom M which can be replaced by C, Si, Ge, Sn. The syntheses of these compounds follow the reaction pattern for the first time established in reference 4:

$$C_2H_5GeCl_3 \xrightarrow{SO_2Cl_2} Cl_3GeCH_2CH_2Cl \xrightarrow{\text{quinoline}} Cl_3GeCH=CH_2 \xrightarrow{CH_3MgBr} (CH_3)_3GeCH=CH_2$$

Furthermore, different possibilities tried out in various publications and previous investigations undertaken by the authors regarding the preparations of these compounds are discussed. In the compounds of the above type M was substituted by C, Si, Ge, and Sn, respectively, and thiocyanogen was joined.

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Relative Reactivities of Some Organic Silicon, Germanium, and Tin Compounds and Their Raman Spectra

SOV/62-59-8-19/42

Data relative to these experiments are to be found in figures 1 and 2. It was shown that the reactivities of the double bonds increase in the order C < Si < Ge < Sn when the central atom M is changed. In a previous paper the authors had found that a change in the reactivities of the double bonds in the molecule is accompanied by a change in the intensities of the Raman frequencies characteristic of these bonds. Therefore, the spectra of the metallic compounds were photographed. The frequencies of the spectrum lines obtained are given and interpreted. The intensities of the respective lines of the double bonds in the Raman spectra exhibit the same order of elements as the reactivities of the said compounds. The distances between poliosymmetrical and deformed lines of the valency oscillations M-C increase according to the geometrical progression ($n = ag^{n-1}$), $g \approx 2$. In the experimental part the syntheses of the individual compounds and the addition reactions are described. It was found in the syntheses that the specific effect of the Cl_3M-group (the β-orientation in chlorination, the tendency towards a β-decomposition, different chlorination

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Relative Reactivities of Some Organic Silicon, Germanium, and Tin Compounds and Their Raman Spectra SOV/62-59-8-10/42

rates) increases considerably at the transition from Si to Ge. The authors conclude by thanking Bugorkova for the determination of the thiocyanogen figures. There are 2 figures, 2 tables, and 27 references, 12 of which are Soviet.

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: November 30, 1957

Card 3/3

5.3700

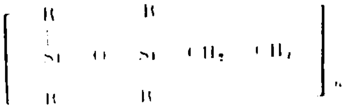
[illegible]

AUTHORS: Polyakova, A. M., Suchkova, M. D., Vdovin, V. M., Mironov, V. F., Korshak, V. V., Petrov, A. D.

TITLE: Concerning the Interaction of Acetylene With Siloxanes and Silanes. Brief Communications

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 12, pp 2257-2259 (USSR)

ABSTRACT: Purified acetylene in reaction with disiloxanes $HR_2SiOSiR_2H$ (where R = CH_3 and C_2H_5) under atmospheric pressure, in presence of chloroplatinic acid in iso-propanol or platinum on carbon, gave polymers in the form of thick oils. IR spectra and other analytical data indicate that the macromolecules of these polymers consist of units:



$$\left[-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-CH_2-CH_2- \right]_n$$

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Concerning the Interaction of Acetylene With Siloxanes and Silanes. Brief Communications

[illegible]

where n = [illegible] to [illegible]. Physical and [illegible] of polymers obtained in [illegible] methyl-, dimethyldiethyl-, and [illegible] are tabulated. In similar reactions, [illegible] lene with methylphenylchlorosilane ([illegible] under atmospheric pressure, in the presence [illegible] platinic acid in isopropanol, [illegible] methylchlorosilyl)ethane $Cl(CH_3)(C_6H_5)SiCH$ [illegible] $(CH_3)Cl$ in 88% yield. Reaction of [illegible] methyldichlorosilane CH_3SiCl_2H gave similarly [illegible] (methyldichlorosilyl)ethane $Cl_2(CH_3)SiCH$ [illegible] in 9% yield; the balance consisted [illegible] starting silane. Acetylene [illegible] any impurities which could [illegible] spectra were taken by N. A. [illegible] 1 table; and [illegible] references, [illegible] Soviet. The U.S. references are: [illegible]

Card 2/3

Concerning the Interaction of Acetylene With Siloxanes and Silanes. Brief Communications

77097
SOV/62-59-12-41/43

Chem. Soc., 78, 1636 (1956); J. L. Speier, D. B. Hook, U.S. Pat. 2823218, 11-02-58.

ASSOCIATION: Institute of Elemento-Organic Compounds, Academy of Sciences, USSR, and N. D. Zelinskiy Institute of Organic Chemistry, Academy of Sciences, USSR (Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR i Institut organicheskoy khimii imeni N. D. Zelinskogo Akademii nauk SSSR)

SUBMITTED: May 25, 1959

Card 3/3

MIRONOV, Vladimir F.

Synthesis and characteristics of silylsubstituted ethylene. In Russian. Gl.hem.dr. 23/24 no.1/2:23-28 '58/59. (EEAI 9:5)

1. Akademiya nauk SSSR, Institut organicheskoy khimii im. Zelinskogo, Laboratoriya khimii, uglevodorov, Moskva.
(Disilabutene)

5(3) SOV/20-124-1-28/69

AUTHORS: Mironov, V. F., Petrov, A. D., Corresponding Member, AS USSR, Pisarenko, V. V.

TITLE: High-Temperature Condensation of Alkyl Dichloro-Silanes With Chloroolefins (Vysokotemperaturnaya kondensatsiya alkildikhlorsilanov s khlorolefinami)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 1, pp 102-104 (USSR)

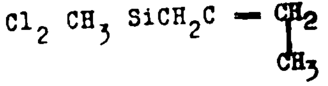
ABSTRACT: The authors present a survey of publications (Refs 1-4) regarding the reaction mentioned in the title. In the present paper it was established that not only $(CH_3)Cl_2SiH$ with vinyl chloride is condensed at 600° to give vinyl methyl-dichloro-silane but that also $(C_2H_5)SiCl_2H$ with vinyl chloride gives vinyl ethyl-dichloro-silane in a 27% yield. This was possible not only in a glass tube but also in an iron tube without considerably affecting the yield. Trialkyl silane, however, cannot be condensed with vinyl chloride as this reaction proceeds according to another scheme. The author further found that the condensation of $(CH_3)Cl_2SiH$ both with cis and trans-dichloro-ethylene gives the same results, namely 20% yields of $Cl_2(CH_3)SiCH{=}CHSi(CH_3)Cl_2$ (structure proved by means of methylation and Raman spectra

Card 1/3

High-Temperature Condensation of Alkyl Dichloro-Silanes With Chloroolefins

SOV/20-124-1-28/69

taken and interpreted by L. A. Leytes and Yu. P. Yegorov). Irrespective of the fact whether methallyl chloride or isocrotyl chloride was used for the condensation, $Cl_2(CH_3)SiCH = C(CH_3)_2$ (about 13%), small amounts of


$Cl_2CH_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$

as well as a mixture of xylenes were isolated on the whole. Allyl chloride can be condensed also with methyl dichloro-silane and forms (30% yield) allyl methyl dichloro-silane. A small amount (in the iron tube a larger one) of propenyl methyl dichloro-silane is then the result. Chloro-aryls can be condensed in an analogous manner, but the saturated halogen alkyls are not able to condense with hydric silanes. Surprisingly, $(CH_3)Cl_2SiH$ reacted with ethylene, mainly vinyl methyl dichloro-silane (14% yield) was formed. A condensation of $ClCF = CF_2$ with $(CH_3)Cl_2SiH$ [illegible] flames and a detonation broke out in the tube above 500^0, thus often causing the tube to be destroyed.

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High-Temperature Condensation of Alkyl Dichloro-Silanes With Chloroolefins

SOV/20-124-1-28/69

A fraction 97 - 100° could however be isolated which probably (according to KRS spectrum) contains $(CH_3)Cl_2SiCF = CF_2$. There are 10 references, 6 of which are Soviet.

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 19, 1958

Card 3/3

SOV 20-128-2-22/59

5(2,3)

AUTHORS: Petrov, A. D., Corresponding Member, AS USSR, Mironov, V. F., Dzhurinskaya, N. G.

TITLE: Addition of Trichlorogermane to Acetylene, Olefines and Their Derivatives in the Absence of Catalysts

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 2, pp 302-304 (USSR)

ABSTRACT: On the basis of the publication survey (Refs 1-4) and the publications by V. A. Ponomarenko and G. Ya. Vzenkova (Ref 6), the authors state that - contrary to other assertions - the addition mentioned in the title proceeds vigorously and under considerable evolution of heat, immediately after mixing the components already at room temperature without any catalysts and initiators. This refers to olefines (1,2) (from ethylene to octene-1), acetylene (3), acrylonitrile (4), allyl acetate (8), allyl chloride (5) and methallyl (6), even vinyl chloride and β-chloro-vinyl-trichloro-silane (9,10). A similar addition of trialkyl silanes to methyl acrylate described by A. D. Petrov and S. I. Sadykh-Zade (Ref 5) is mentioned. Table 1 indicates the yields and properties of the compounds

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[illegible]

Addition of Trichlorogermane to Acetylene, Olefins and Their Derivatives in the Absence of Catalysts

obtained: β-cyano-ethyl-trichlorogermane, γ-chloro-propyl-trichlorogermane, γ-chloro-isobutyl-trichlorogermane, 1(trichlorogermyl)-2(trichlorosilyl)-ethane, 1,2-bis (trichlorogermyl)-ethane, ethyl trichlorogermane, n-octyl trichlorogermane, γ-(trichlorogermyl) propyl acetate. Sometimes, the yields of the addition products were higher than those indicated in respective publications for addition with catalysts. As is known (Ref 7), the addition of silicon chloroform to the substances indicated in table 1 mostly proceeds only in the presence of catalysts. Without a catalyst, it is only possible exceptionally and under severe conditions. Thus, it becomes evident that the trichlorogermane, in a wide range of addition reactions, is much more active than the trichlorosilane. There are 1 table and 7 references, 5 of which are Soviet.

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: May 28, 1959

Card 2/2

MIRONOV, V F

83478

S/190/60/002/009/009/019
B004/B060

53700C also 2109, 2209

AUTHORS: Korshak, V. V., Polyakova, A. M., Sakharova, A. A., Mironov, V. F., Chernyshev, Ye. A.

TITLE: Polycondensation of Halogen Alkyl (Halogen Aryl) Halogen Silanes Under the Action of Metallic Sodium

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 9, pp. 1370-1374

TEXT: The authors carried out condensation reactions with the following five compounds: $ClSi(CH_3)_2CH_2Cl$; $ClSi(CH_3)(C_6H_5)CH_2Cl$; $ClSi(CH_3)(C_2H_5)CH_2CH_2CH_2Cl$; $ClSi(CH_3)_2C_6H_4Cl$, and $ClSi(CH_3)_2OSi(CH_3)_2CH_2CH_2Cl$. The reactions took place in nitrogen current with metallic sodium suspended in toluene as a catalyst. The molecular weight was cryoscopically determined in benzene. A table supplies the molecular weights of the condensates, the polymerization coefficients, yields, and silicon content. The temperature dependence of the viscosity of polymer $[-Si(CH_3)_2CH_2-]_n$

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83478

Polycondensation of Halogen Alkyl (Halogen Aryl) Halogen Silanes Under the Action of Metallic Sodium

S/190/60/002/009/009/019
B004/B060

and of polymer $[-Si(C_6H_5)(CH_3)CH_2-]_n$ is illustrated in a diagram. Despite a lower degree of polymerization, the presence of the phenyl group gives rise to a higher viscosity. The authors analyzed the resulting compounds for the presence of -Si-Si- bonds by treating with concentrated potash lye and piperidine according to A. P. Kreshkov's method (Ref. 8). No such bonds were detected in any of the reaction products obtained. The authors, therefore, assume a succession of -Si-C- bonds. There are 1 figure, 1 table, and 11 references: 4 Soviet, 6 US, and 1 German.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental-organic Compounds of the AS USSR)

SUBMITTED: April 4, 1960

Card 2/2

81600

S/062/60/000/04/06/006
B004/B066

53700

AUTHORS: Mironov, V. F., Shchukovskaya, L. L.

TITLE: Relative Reactivity of Some Alkenyl Silanes During Their Interaction With Trichloro Silane

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 4, pp. 760 - 762

TEXT: According to Refs. 1 - 3, hydrosilanes were added to vinyl and allyl silanes under conditions which required the performance of the reaction in an autoclave. The authors used the catalyst of I. L. Speier (Ref. 4) (0.1 N $H_2PtCl_6 \cdot 6H_2O$ in isopropanol). The reaction could thus be carried out at room temperature in a glass vessel. The relative reactivity was investigated by allowing equimolecular mixtures of allyl and vinyl silanes to react with an equivalent trichloro silane, and by determining the quantity of the reacting initial substance. The following was found: Vinyl trichloro silane reacted to 60%, allyl trichloro silane to 40% only; in the case of $Cl_3SiCH=CH_2$ and $(C_2H_5)_2CH_3SiCH=CH_2$,

Card 1/2

81600

Relative Reactivity of Some Alkenyl Silanes During Their Interaction With Trichloro Silane

S/062/60/000/04/06/006
B004/B066

the former compound reacted to 23%, the latter to 77%; in the case of $Cl_3SiCH_2CH=CH_2$ and $(CH_3)_3SiCH_2CH=CH_2$, the former compound reacted to 60%, the latter to 40%. The accumulation of chlorine atoms at the silicon atom thus facilitates the addition of trichloro silane to allyl-substituted silane and inhibits this reaction in vinyl-substituted silane. A table presents the ten compounds synthesized for the first time and their physical data, among them α,ω-disilyl ethanes which were obtained by addition of hydride silanes to various vinyl silanes and by alkylation by means of RMgX or ArMgX. The authors refer to papers by A. V. Topchiyev et al.(Ref. 2) and A. D. Petrov et al.(Ref. 6). There are 1 table and 6 references: 3 Soviet, 1 Japanese and 2 American.

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), Institut khimii silikatov Akademii nauk SSSR (Institute of Silicate Chemistry of the Academy of Sciences, USSR)

SUBMITTED: August 19, 1959

Card 2/2

KARTSEV, G.N.; SYRKIN, Ya.K.; MIRONOV, V.F.

Dipole moments of some germanium organic compounds. Izv.AN SSSR Otd.khim.nauk no.5:948-949 My '60. (MIRA 13:6)

1. Institut tonkoy khimicheskoy tekhnologii imeni M.V. Lomonosova.
(Germanium organic compounds--Dipole moments)

82693

S/062/60/000/008/007/012
B004/B054

5.3700

AUTHORS: Mironov, V. F. and Nepomnina, V. V.

TITLE: Synthesis of Alkenyl Silanes by Addition of Methyl dichloro Silane to Diene- and Acetylene Compounds

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 8, pp. 1419-1423

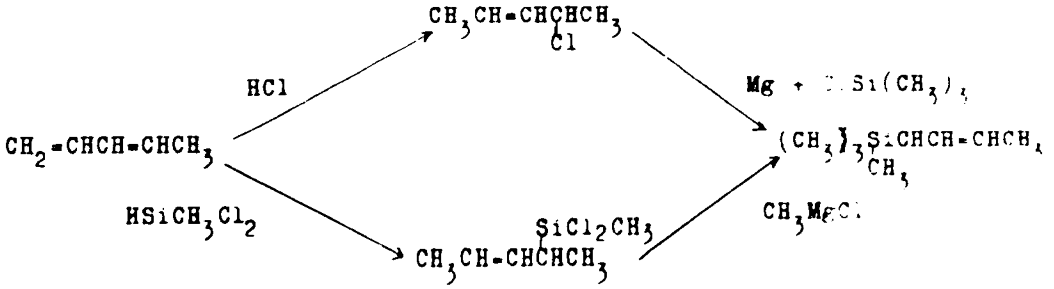
TEXT: Other investigators (Refs. 1, 3) arrived at the conclusion that trichlorosilane and methyl- or ethyl-dichloro silane are added to butadiene in 1,4-position only. The authors found that this also applies to the addition of methyl-dichloro silane to piperylene. The structure of the reaction product could be established by the identity of the Raman spectrum of the compound obtained in the following two ways:

Card 1/4

82693

Synthesis of Alkenyl Silanes by Addition of Methyl-dichloro Silane to Diene- and Acetylene Compounds

S/062/60/000/008/007/012
B004/B054



Instead of platinum on carbon, the authors used J. L. Speier's (Ref. 9) catalyst for their syntheses, and thus could work under mild conditions at atmospheric pressure. With addition of methyl-dichloro silane to diallyl an isomer with a different position of the double bond is formed besides the ε-hexenyl-methyl-dichloro silane expected, which was established by means of the Raman spectrum after methylation of the compounds. Further, the authors performed the following syntheses: addition of methyl-dichloro silane to phenyl acetylene:

Card 2/4

82693

Synthesis of Alkenyl Silanes by Addition of Methyl-dichloro Silane to Diene- and Acetylene Compounds

S/062/60/000/008/007/0?2
B004/B054

$$C_6H_5C\equiv CH + HSiCl_2CH_3 \longrightarrow C_6H_5CH{=}CHSiCl_2CH_3 \xrightarrow{CH_3MgCl} C_6H_5CH{=}CHSi(CH_3)_3.$$

The β-(trimethylsilyl)-styrene thus obtained differs in its Raman spectrum from the α-isomer produced formerly (Ref. 17). Besides, the β-isomer was also produced by means of organomagnesium reaction (Ref. 18); here $C_6H_5C\equiv CSi(CH_3)_3$ was formed as a by-product. The addition of methyl-dichloro silane to hexine occurs with the formation of the α-isomer which was identified by the Raman spectrum: $C_4H_9C\equiv CH + HSiCl_2CH_3 \rightarrow C_4H_9CH{=}CHSiCl_2CH_3 \longrightarrow C_4H_9CH{=}CHSi(CH_3)_3$. Further, the reaction was carried out with ethyl-dimethyl-ethinyl silane: $C_2H_5(CH_3)_2SiC\equiv CH + HSiCH_3Cl_2$

$$\longrightarrow C_2H_5(CH_3)_2SiCH{=}CHSiCH_3Cl_2 \xrightarrow{CH_3MgCl} C_2H_5(CH_3)_2SiCH{=}CHSi(CH_3)_3.$$

The physical data and the Raman spectrum confirmed the structure of this compound as a 1,2-disubstituted ethylene (Ref. 2). The addition of

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82693

Synthesis of Alkenyl Silanes by Addition of Methyl-dichloro Silane to Diene- and Acetylene Compounds

S/062/60/000/008/007/012
B004/B054

methyl-dichloro silane to isopropoxy acetylene is also mentioned. The silyl group is always added to the C≡C bond. The authors thank L. Leytes for taking and analyzing the Raman spectra. There are 26 references: 15 Soviet, 10 US, and 1 British.

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 27, 1959

Card 4/4

86480

5.3770 2209 1290 1273

S/062/60/000/011/007/016
B013/B078

AUTHORS: Mironov, V. F., Pogonkina, N. A.

TITLE: Relative Reactivity of ω-Trialkylsilyl-substituted Alcohols and Mercaptans With Phenyl Isocyanate

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 11, pp. 1998 - 2002

TEXT: The authors study the reactivity of organosilicon alcohols and mercaptans of the following homologous series: $(CH_3)_3Si(CH_2)_nOH$ and $(C_2H_5)_2CH_3Si.(CH_2)_nSH$, n = 1, 2, and 3. For this purpose, an equivalent amount of phenyl isocyanate was added to certain amounts of the organosilicon alcohol-methanol mixture concerned. The molar portion of the reacting organosilicon alcohol was calculated by analyzing the silicon content in the resulting urethan mixture. The results obtained for three organosilicon alcohols are given in Table 1. It may be seen from them that trimethyl-silyl methanol is 2.5 times more reactive than methyl alcohol, and about twice more active than the homologs coming next to it:

Card 1/3

86480

S/062/60/000/011/007/016
B013/B078

Relative Reactivity of ω-Trialkylsilyl-substituted Alcohols and Mercaptans With Phenyl Isocyanate

β-trimethyl-silyl ethanol and γ-trimethyl-silyl propanol. Also the reactivity of organosilicon mercaptans of the homologous series $(C_2H_5)_2CH_3Si(CH_2)_nSH$ was examined and calculated by the same method, with respect to butyl mercaptan. Results are given in Table 2. Diethylmethyl silyl-methyl mercaptan exhibited only about half the reactivity of butyl mercaptan, and about one-tenth of the reactivity of the homologs coming next to it and having the thiol group in the β- and γ-positions. The results obtained can be explained by a rapid extinction of the positive induction effect of the electron-emitting trialkyl-silyl group. This effect is obviously strongest in compounds with functional groups in the α-position. The special character of the compounds with functional groups in the α-position is also observable in the analysis of the Raman spectra of the alcohols and mercaptans concerned. The organosilicon mercaptans used were synthesized by the method described in Ref.4, except for γ-trimethyl-silyl propanol. The latter was synthesized as follows:

Card 2/3

86480

Relative Reactivity of ω-Trialkylsilyl-substituted Alcohols and Mercaptans With Phenyl Isocyanate

S/062/[illegible]
[illegible]

$CH_2{=}CHCH_2C_2CCH_2 \xrightarrow{CH_3Cl_2SiH} CH_3Cl_2SiCH_2CH_2CH_2OCOCH_3 \xrightarrow{CH_3MgCl} (CH_3)_3SiCH_2CH_2CH_2OH$

In view of the high yield and purity of the product, this method seems to be better than the one described in Ref. 5. The Raman spectra were taken by L. A. Leytes with an ИСП-51 (ISP-51) apparatus. There are 2 tables and 8 references: 3 Soviet and 5 US.

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: May 29, 1959

Card 3/3

86482

5.3770

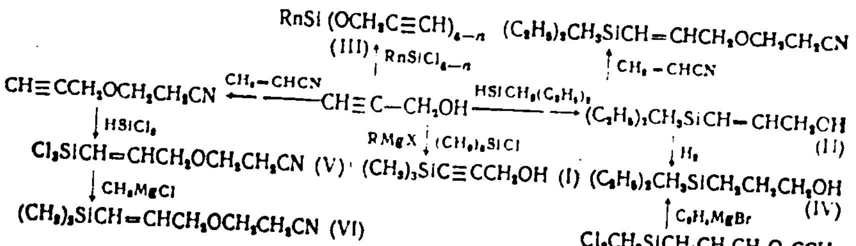
S/062/60/000/[illegible]
B013/[illegible]

AUTHORS: Mironov, V. F., Maksimova, N. G.

TITLE: Synthesis of Unsaturated Organosilicon Compounds on Propargyl Alcohol Bases

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 11, pp. 2059 - 2061

TEXT: This is a brief report on the investigation of the conversions of propargyl alcohol according to the scheme attached:

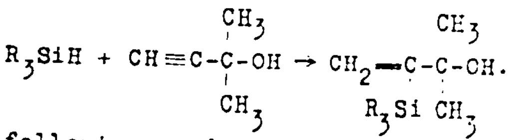


86482

Synthesis of Unsaturated Organosilicon Compounds on Propargyl Alcohol Bases

S/062/60/000/011/013/016
B013/B078

Special reference is made to the order of addition of R_3SiH to propargyl alcohol, which does not agree with the order of addition of these silicohydrides on $(CH_3)_2C(OH)C\equiv CH$ (Refs. 2 and 3).



$R_3SiH + CH\equiv C-\underset{CH_3}{\overset{CH_3}{C}}-OH \rightarrow CH_2=\underset{R_3Si}{C}-\underset{CH_3}{\overset{CH_3}{C}}-OH$. Proceeding from propargyl alcohol, the following products were obtained: γ-(trimethyl silyl)propargyl alcohol (I) - $C_6H_{12}SiO$ - boiling point 65°C (10 mm) - yield 43.5%. γ-(diethyl methyl silyl)allyl alcohol (II) - $C_8H_{18}SiO$ - boiling point 99°-100°C (10 mm) - yield 67.5%. The products of the addition of acrylonitrile to alcohol (II) yielded $C_{11}H_{21}SiNO$ - boling point 155°C (20 mm) - yield 60%. γ-(diethyl methyl silyl)propyl alcohol (IV) - $C_8H_{20}SiO$ - boiling point 86°C (3 mm). Although the refractive index and boiling point of this alcohol somewhat diverge from the established

Card 2/4

86462

Synthesis of Unsaturated Organosilicon Compounds on Propargyl Alcohol Basis

S/062/[illegible]
B0[illegible]/[illegible]

γ-(diethyl methyl silyl)propargyl alcohol [illegible], the Raman spectra coincide with the exception of the weakest lines. Propargyl oxytrimethyl silane (III) $C_6H_{12}SiO$ - boiling point 110.8°C ([illegible] mm) - yield [illegible]%. In a similar manner were synthesized: $C_2H_5(CH_3)_2SiOCH_2C\equiv CH$ - boiling point [illegible]°C (745 mm); $(CH_3)_2Si(OCH_2C\equiv CH)_2$ - boiling point 75°C (1[illegible] mm); $C_2H_5Si(OCH_2C\equiv CH)_3$ - boiling point 118°C (10 mm).

β-(γ-trichlorosilyl allyloxy)propionitrile (V) - $C_6H_8NOCl_3Si$ - boiling point 140°C (7 mm). The methylation of CH_3MgCl leads to β-(γ-trimethyl silyl allyloxy)propionitrile (VI) - boiling point [illegible]°C (6 mm) - yield 50%. The Raman spectra were taken by L. A. Leytes. A. D. Petrov and M. F. Shostakovskiy are mentioned. There are 1[illegible] Soviet references.

X

Card 3/4

86482

Synthesis of Unsaturated Organosilicon Compounds on Propargyl Alcohol Bases

S/062/60/000/011/013/016
B013/B078

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 26, 1960

Card 4/4

86484

53710

S/062/
B0

AUTHORS: Mironov, V. F., [illegible]

TITLE: Reaction of Allyl Halides With Trichlorogermane

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 11, p. 2066

TEXT: In this "Letter to the Editor" the authors report on the reaction of allyl halides with trichlorogermane. A new reaction of trichlorogermane with allyl bromide and allyl chloride was discovered, which leads to the formation of allyl trichlorogermane according to formula (1): $CH_2 = CHCH_2X + HGeCl_3 \rightarrow CH_2 = CHCH_2GeCl_3 + HX$. Allyl trichlorogermane has been first obtained by direct synthesis from allyl chloride and germanium (Ref. 1). Its properties are: Boiling point 155.5°C (756 mm), n_D^{20} 1.4938, d_4^{20} 1.5480. $HGeCl_3$ is known to differ from $HSiCl_3$ by its higher reactivity. With a simple [illegible] at room temperature it adds to the multiple bonds of various olefins

Card 1/2

Reaction of Allyl Halides With Trichlorogermane S/062/60/000/011/[illegible]
86484
B013/B078

and their derivatives even without a catalyst (Refs. 2 and 3): $CH_2{=}CHCH_2Cl + HGeCl_3 \rightarrow ClCH_2CH_2CH_2GeCl_3$ . . . (2). When $HGeCl_3$ was added to allyl bromide the reaction proceeded, however, according to formula (1). Thus, allyl trichlorogermane with a yield of 37% was obtained from allyl bromide. Also, when $HGeCl_3$ was added to allyl chloride the reaction proceeded according to formula (1) provided this was done in ether. The yield in this case amounts to 17%. It is noted that a similar reaction of $HSiCl_3$ with allyl chloride has been known in technical literature (Refs. 4 and 5); however, it takes place only at very high temperatures (600°C) in the gaseous phase, whereas the above-described reaction took place in the liquid phase at room temperature. There are 5 Soviet references.

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 26, 1960

Card 2/2

57166

5 3700 2203 [illegible] 136

AUTHOR: [illegible]

TITLE: [illegible]

ORIGINAL [illegible]

TEXT: [illegible] silane [illegible] $N H_2$ [illegible] H_2 [illegible] silane and [illegible] chloride. This method has the advantages of simple [illegible] and the possibility of adding new hydr[illegible] silanes in which the [illegible]

Card 1/2

[illegible]156

Synthesis of Unsaturated Organ[illegible]
by Dehydrochlorination of γ-Chlor[illegible]
Silane Chlorides

atom) to hal[illegible]olefins. Th[illegible] effected [illegible] [illegible] also added CH_3Cl_2SiH to [illegible]

silane chlorides listed in Table [illegible] The [illegible] dehydrochlorination of (γ-chl[illegible]alkyl) silane chlorides [illegible] chlorides. It was found that 5-10% piperidine relative to [illegible] silane chloride is sufficient to attain maximum yields of alkenyl [illegible] chlorides. The (γ-chlor[illegible]alkyl) silane chlorides given in [illegible] hydrochlorinated in this manner. This method is [illegible] and most convenient way of synthesizing [illegible] methallyl methyl dichlorosilane and [illegible] following [illegible] exception of [illegible]

always yielded a mixture of [illegible] of these two alkenyl [illegible] the [illegible] silanes during distillation [illegible], however, [illegible]

[illegible]

87166

Synthesis of Unsaturated Organosilicon Compounds by Dehydrochlorination of (γ-Chloro-alkyl) Silane Chlorides

S/062/[illegible]

evidently most easily split off from compounds of the (γ-chloro-alkyl)-[illegible] chloro-silane type. (β-chloro-ethyl) trichloro silane and (β-chloro-ethyl) dichloro silane split off HCl much less readily under the action of piperidine. (γ-chloro-alkyl) silane chlorides behave similarly. The reverse dependence was observed under the action of quinoline, however. There are 3 tables and 13 references: 11 Soviet and 2 US.

ASSOCIATION: Institut [illegible]
[illegible]

SUBMITTED: June 7, [illegible]

Card 2/2

87167

S/062/60/000/012/004/020
B013/B055

15 8116

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

TITLE: New Method for the Preparation of Organosilicon Monomers by High-temperature Condensation of Alkenyl Chlorides, Aryls and Olefins With Hydrosilanes (Expression used to denote silanes in which the silicon contains at least one unsubstituted hydrogen)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 12, pp. 2147-2156

TEXT: The present publication treats the investigation of high-temperature condensation as a method of preparing organosilicon monomers. A method for the synthesis of vinyl silane chlorides (the expression "silane chloride" is used by the author to denote that all available hydrogen atoms bound to silicon are replaced by chlorine) was developed at the Laboratoriya khimii uglevodorodov Instituta organicheskoy khimii AN SSSR (Laboratory of Hydrocarbon Chemistry of the Institute of Organic Chemistry AS USSR). Its practical realization, however, meets with difficulties. For this reason

Card 1/4

87167

New Method for the Preparation of Organosilicon S/062/60/[illegible]
Monomers by High-temperature Condensation of B013/B05[illegible]
Alkenyl Chlorides, Aryls and Olefins With
Hydrosilanes

√

The authors at the same time investigated another method, the uncatalyzed high-temperature condensation, basing their study on publications by C. L. Agry (Refs. 4, 6). In this investigation, which was started in 19[illegible], the authors tested the general validity of the reaction described by Agry and extended it to complicated hydrosilanes (Refs. 8, 10-17). The optimal conditions for this reaction were found to be 580-590 °C and a contact time of 20-25 sec. The simplicity of the required apparatus, accessibility of materials, safety and high yields render this reaction one of the most convenient of the existing methods for synthesizing vinyl silane chlorides. The authors studied the high-temperature condensation with vinyl chloride of all the hydrosilanes of the series $HSiR_nCl_{3-n}$ (n = 0, 1, 2, and 3). Yields of up to 90% were obtained with trichloro silane (n = 0). Trialkyl silanes (n=3) gave no condensation reaction (Fig. 1). This compound gave a different reaction which the authors termed a reduction to distinguish it from the condensation: $R_3SiH + ClCH{=}CH_2 \rightarrow R_3SiCl + CH_2{=}CH_2$. The authors also discovered a new type of inter[illegible] between [illegible] silanes and olefins (ethylene

Card 2/4

97167

New Method for the Preparati [illegible] S/0 2 [illegible]
Monomers by High-temperature Condensation of [illegible]
Alkenyl Chlorides, Aryl [illegible]
Hydrosilanes

and propylene)(F [illegible] the [illegible]
chemistry of silicon. CH_2-CH_2 + HS [illegible] $\longrightarrow$ [illegible]

the investigation carried out the high temperature condensation of hydro-
chlorosilanes ($HSiCl_3$, $RSiCl_2H$) with mono- and poly- [illegible] chlorides [illegible]

claimed to constitute a new, generally [illegible] of
synthesizing unsaturated organosilicon monomers (Table [illegible]). Fundamentally,
the reaction is an entirely new way of forming [illegible]
described as homolytic silylation. Apart from the [illegible]
the synthesis of aromatic organosilicon monomers, [illegible]
fourth method, the reaction of hydrosilanes with aryl [illegible]
peratures (550-700°C) and atmospheric pressure, [illegible]
(condensation): RCl + $HSiR'Cl_2$ $\longrightarrow$ $RSiCl_2$ [illegible] + HCl; [illegible]

C_6H_5; [illegible]

20-33). They are given in generalized form in this work [illegible]
type have been patented (Refs 34, 35), the necessity of a catalyst being
indicated in both publications. The authors, however, were [illegible]
Card 3/4

87167

New Method for the Preparation of Organosil[illegible]
Monomers [illegible]
Alkenyl Chlorides, [illegible] With
Hydrosilanes

[illegible] The reaction [illegible] empty heated [illegible] passing [illegible] rate, hydrosilane mixture [illegible] permitting [illegible] of 10 to 100 sec. This enables the reaction to be performed in a continuous process. The material of the tube [illegible]. Yields of various aryl chlorosilanes obtained in this manner are given in Table 2. The method can be applied for the preparation of [illegible] silanes with 2 or 3 chlorine atoms bonded to silicon. Moreover yields are about equal to and in some cases even higher than the yields obtained in the catalytic reaction of aromatic compounds with hydrosilanes. There are [illegible] figures, 2 tables, and 37 references: [illegible] 1 Czechoslovakian.

ASSOCIATION: Institut [illegible] nauk SSSR (Institute [illegible] Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: June 27, 1959, supplemented September 21, 19[illegible]

Card 4/4

[illegible]
B[illegible]/B[illegible]

AUTHORS: Freydlin, L. Kh., Zhukova, I. F., and Mironov, V. F.

TITLE: Study of the Hydrogenation Rate of Vinyl and Allyl Compounds of Carbon, Silicon, Germanium and Tin on a Skeleton Nickel Catalyst

PERIODICAL: Izvestiya Akademii nauk SSSR. [illegible] nauk, [illegible], No. [illegible], pp. [illegible]

TEXT: The authors briefly report on a study of the reactivity of α- and β-ethylene bonds in the following compounds: $(CH_3)_3CCH=CH_2$, $(CH_3)_3SiCH=CH_2$, $(CH_3)_3GeCH=CH_2$, $(C_2H_5)_3SnCH=CH_2$ and $(CH_3)_3CCH_2CH=CH_2$, $(CH_3)_3SiCH_2CH=CH_2$, $(CH_3)_3GeCH_2CH=CH_2$, $(C_2H_5)_3SnCH_2CH=CH_2$. The skeleton catalyst was prepared by lixiviating a Ni Al melt [illegible] with [illegible]% alkali lye. The reaction rate was characterized by the rate of hydrogen absorption as a function of time (Fig. [illegible]) and the half life period $t_{1/2}$ of the reaction. Reading was performed in intervals of [illegible] seconds each. The investigation

Card 1/[illegible]

Study of the Hydrogenation Rate of Vinyl- and [illegible]
Allyl Compounds of Carbon, Silicon, Germanium, [illegible]
and Tin on a Skeleton Nickel Catalyst

showed that the reaction rate of the [illegible] skeleton nickel catalyst [illegible] in the radical polymerization [illegible] > Sn [illegible] vinyl compounds [illegible] hydrogenation [illegible] than allyl [illegible] Vinyl and allyl [illegible] similar way. Carbon [illegible] of [illegible], [illegible] and [illegible]

ASSOCIATION: Institut [illegible] khimii [illegible] Akademii nauk SSSR [illegible]
N. D. Zelinskiy [illegible] the Academy [illegible] USSR

SUBMITTED: May [illegible] 60

Card [illegible]

MIRONOV, V. F.

New method for the synthesis of unsaturated silicon organic compounds by high-temperature condensation of olefins and chloroolefins with silanes. Coll Cz Chem 25 no.8:2167-2172 Ag '60.
(EEAI 10:9)

1. Institut organicheskoy khimii im. N.D. Zelinskogo, Akademiya nauk SSSR, Moskva.

(Silicon) (Olefins) (Silanes) (Chlorine) (Organic compounds)

5.3700(B)
~~5(2), 5(3)~~

68814
S/020/60/131/01/027/060
B011/B006

AUTHORS: Mironov, V. F., Dzhurinskaya, N. G., Petrov, A. D., Corresponding Member, AS USSR

TITLE: Addition of $HGeCl_3$ to Halogen Substituted Ethylene Derivatives. Dehydrochlorination of α,β-Dichloroethyltrichlorogermane

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 1, pp 98-100 (USSR)

ABSTRACT: The authors investigated the addition of $HGeCl_3$ to various chlorine substituted derivatives of ethylene (from $ClCH=CH_2$ to $Cl_2C=CCl_2$), which hardly add $HSiCl_3$. In the present paper, the authors proved, that trichlorogermane, however, adds to dichloro-, trichloro-, and tetrachloroethylene in a completely uncatalyzed reaction. The addition proceeds under slight spontaneous heating. If vinyl chloride is bubbled through $HGeCl_3$ the addition is accompanied by more intense spontaneous heating. The most astonishing result obtained was that no α-, but only β-chloroethyltrichlorogermane (33%) was formed (see

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Addition of $HGeCl_3$ to Halogen Substituted Ethylene Derivatives. Dehydrochlorination of α, β-Dichloroethyltrichlorogermane

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scheme). In this connection, the sequence of the addition of $HSiCl_3$ to vinyl chloride was investigated. It was found that $HSiCl_3$ and CH_3Cl_2SiH likewise, can only be added to vinyl chloride by reacting in an autoclave, despite the presence of a catalyst as highly active as chloroplatinic acid, yielding only 6% α-chloroethyltrichlorosilane (see scheme). The authors have thus proved that the sequence observed in the addition of $HGeCl_3$ to vinyl chloride is different from the one in trichlorosilane addition. The reaction mechanisms are evidently different in the two cases. The dehydrochlorination of α,β-dichloroethyltrichlorogermane was effected both by means of quinoline and aluminum chloride. The authors previously (Refs 5,6) investigated a similar dehydrochlorination by the two latter reagents for an analogous organosilicon compound, $Cl_3SiCHCl\cdot CH_2Cl$. Now it was found that the rules observed then are also valid in the present case, i.e. that quinoline splits off the β-chlorine atom, and aluminum chloride the α-chlorine

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Addition of $HGeCl_3$ to Halogen Substituted Ethylene Derivatives. Dehydrochlorination of α,β-Dichloroethyltrichlorogermane

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atom (see scheme). In the case of α,β-dichloroalkyltrichlorosilanes the mechanism of dehydrochlorination by means of aluminum chloride was formerly (Refs 7,8) explained by rearrangement of the β-carbonium ion formed, involving a shift of the trichlorosilyl group from the α-carbon atom to the β-carbon atom. The authors believe that a similar rearrangement mechanism occurs in the present case (see scheme). Experiments to split off HCl from $Cl_3SiCH_2CHClGeCl_3$ with the aid of quinoline only resulted in β-decomposition (see scheme). After some hours, α-chlorovinyltrichlorogermane autopolymerizes to a milky, opaque solid (Refs 6,9). Only three of the chlorine atoms of β-chlorovinyltrichlorogermane are hydrolyzed by titration with 0.1 N alkali solution. Decomposition accompanied by liberation of acetylene (Ref 11) does not occur in this case. The properties of the five germanium compounds synthesized for the first time are listed in table 1. L. A. Leytes took the spectra of these compounds. There are 1 table and 13 references, 10 of which

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Addition of $HGeCl_3$ to Halogen Substituted Ethylene Derivatives. Dehydrochlorination of α, β-Dichloroethyltrichlorogermane

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are Soviet.

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

SUBMITTED: November 23, 1959

Card [illegible]/4

MIRONOV, V. F.

Doc Chem Sci - (diss) "Carbo-functional organic compounds of silicon and germanium." Moscow, 1961. 40 pp; (Academy of Sciences USSR, Inst of Petrochemical Synthesis); 280 copies; free; list of author's works at end of text; (KL, 10-61 sup, 206)

MIRONOV V F

PHASE I BOOK EXPLOITATION SOV/5606

Petrov, Aleksandr Dmitriyevich, Vladimir Florovich Mironov, Vasiliy 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: L. 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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Synthesis of Organosilicon Monomers SOV/5606

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. Freydlina, 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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PART I. INTRODUCTION TO THE CHEMISTRY OF ORGANOSILICON COMPOUNDS

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Synthesis of Organosilicon Monomers SOV/5606

PART III. METHODS OF SYNTHESIZING AROMATIC AND ALIPHATIC-AROMATIC ORGANOSILICON MONOMERS

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7

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5 3700 1273 2209 1915 S/192/61/002/005/002/005
D202/D304

AUTHORS: Yegorov, Yu.P., Leytes, L.A. and Mironov, V.F.

TITLE: A comparative study of combined dispersion spectra of alkyl silanes, germanates and stannates

PERIODICAL: Zhurnal strukturnoy khimii, v.2, no.5, 1961, 562-568

TEXT: This is a continuation of previous studies, in which the authors investigated the spectra of similar carbon and silicon compounds and showed that the Si atom is affected by double bonds which are in the β-position, and that in tetra-substituted silanes the substituting groups do not interact with each other. This leads to the presence in the vibrational spectra of these compounds of such frequencies which are pertinent to each substituting group (alkyl, alkenyl or aryl). X

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A comparative study ... [illegible]/002/005/[illegible]/00
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In the present study, the authors investigated the combined dispersion spectra of 3 allyl germanates and of the allyl stannate. It was found that an allyl group joined to a Ge or Sn atom possesses a summary of characteristic frequencies as in the case of a Si atom, the intensity of corresponding lines rising additionally with the number of allyl groups; by substituting the C atom with that of Si, Ge, or Sn a general spectrum change consists of a marked rise of those line intensities which depends on the vibrations of the central M atom, while their frequencies are lowered; this indicates that the interaction of the atom M with an allyl double bond in the β-position increases in the series Si, Ge, Sn, the line-intensity corresponding to the C = C bond increasing in approximately geometrical progression. In the present work, the authors studied the combined dispersion spectra (CD) of $(CH_3)_3 - Ge - CH_2 - CH = CH_2$, $(CH_3)_2 - Ge - (CH_2 - CH = CH_2)_2$, $CH_3 - Ge - (CH_2 - CH = CH_2)_3$,

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A comparative study ...

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$(CH_3)_3 - Sn - CH_2 - CH - CH_2$. They also repeated the spectrum investigation of $(CH_3)_3C - CH_2 - CH = CH_2$ which was published previously. The CD spectra were obtained on the apparatus ИСП (ISP)-51 with a medium camera; frequencies were checked with an Fe arc spectrum on the ИЗА (IZA)-2 comparator; the maximum line intensities were determined with МФ (MF)-2 and MF-4 micro-photometers, by a method given previously; the intensities being expressed on the cyclohexane scale, that of cyclohexane lines maximum 802 cm^{-1} was taken as 250 units. As a control standard the authors used the $(CH_3)_3 - Si - CH_2 - CH = CH_2$ spectrum which they determined precisely previously. For calculating the intensities in respect of an equal number of molecules in the dispersing volume they used the following equation: $I_M = I_o d_o M_c / d_c M_o$, where I_M is the intensity for an equal molecular number in the dispersing volume, I_o the intensity for a

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A comparative study ... S/[illegible]/002/[illegible]
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unit volume and d_0 and d_c the densities of cyclo-hexane and of the investigated compound respectively, and M_0 and M_c the molecular weights of cyclo-hexane and of the compound. The authors also determined the degree of depolarization of the most intensive CD lines by covering the vessel with the dispersing compound with a cylinder of polaroid film. These determinations were only semiquantitative. The spectra of the investigated compounds are given, together with the coefficient $K = \frac{d_0 M_c}{M_0 d_c}$ for intensity calculations for an equal number of molecules in the dispersing volume. Assuming that compounds of the $(CH_3)_3M - CH_2 - CH = CH_2$ type belong to the space group C_{3V} and exhibit two symmetric frame rotations of the A_1 type and one of the E type, the authors determined the frequencies of these frame vibrations, the intensities in their line

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A comparative study ... S/192/61/002/005/002/005
D202/D304

maxima, the integral intensities and the degree of depolarization; the integral intensities are determined on the ISP-51 apparatus with an additional FEP attachment and expressed in the cyclohexane scale, the integral cyclohexane line 802 cm^{-1} being taken as 500 units. The results are given in a table. The following scheme is proposed for the changes in alkyl germanates frame vibration frequencies, taking place during the change of symmetry: $(CH_3)_4$ Ge $\rightarrow$ $(CH_3)_3$ Ge $- CH_2 - CH = CH_2$

Tel C_{3V}

$\rightarrow (CH_3)_2 - Ge - (CH_2 - CH = CH_2)_2 \rightarrow CH_3\ Ge - (CH_2 - CH = CH_2)_3$

C_{2V} C_{3V}

There are 4 tables, 1 figure and 22 references: 13 Soviet-bloc and 9 non-Soviet-bloc. The references to the 4 most recent English-language publications read as follows: W.F.Edgell,

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A comparative study ...

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C.H. Ward, J. Amer. Chem. Soc. 77, 6400, (1955); D.N. Waters, L.A. Woodward, Proc. Roy. Soc., A246, 119, (1958); D.P. Craig, J.Chem. Soc. 332 (1954); J. Chatt, A.A. Williams, J. Chem. Soc. 4403 (1954)

ASSOCIATION: Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR (Institute of Organic Chemistry im. N.D. Zelinskiy AS USSR)

SUBMITTED: November 18, 1960

Card 6/6

MIRONOV, V.F.; NEPOMNINA, V.V.

Effect of the character of the silyl group on the rate of dehydrochlorination of some β- and γ-chloroalkychlorosilanes by piperidine. Izv.AN SSSR.Otd.khim.nauk no.5:920-921 My '61. (MIRA 14:5)

1. Institut organicheskoy khimii im. N.D.Zelinskogo.
(Silyl group) (Silane) (Piperidine)

S/661/61/000/006/023/081
D205/D302

AUTHORS: Mironov, V. F. and Nepomnina, V. V.

TITLE: The rearrangement of α-β-dichloro-iso-propyl trichlorosilane on dehydrohalogenation with aluminum chloride

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, 112-116

TEXT: α-β-dichloro-iso-propyl trichlorosilane was dehydrohalogenated by $AlCl_3$, giving a product which was identified as β-chloropropenyl trichlorosilane. This is an additional proof for the proposed mechanism

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The rearrangement of ...

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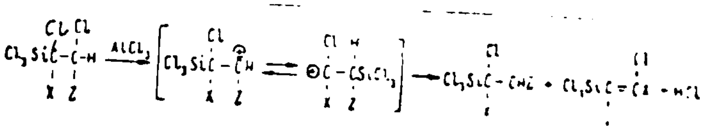
D205/D302



I. A. Shikhiyev (Baku), R. Kh. Freydlina (INEOS AN SSSR, Moscow), P. S. Rościszewski (Institute of Synthetic Resins, Warsaw) and A. L. Klebanskiy (VNIISK, Leningrad) took part in the discussion. The opinion expressed by the investigators, who took part in the discussion, was that the proposed mechanism is not sufficiently clear for the time being and further, more substantial proof is needed. There are 2 Soviet-bloc references.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR, Moskva (Institute of Organic Chemistry, Academy of Sciences, Moscow)

Card 2/2

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 silicon-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: $>Si-(CH_2)_nCl$ (I), $>Si(CH_2)_n$ $CH=CH_2$ (II) and $>Si(CH_2)_n \cdot C_6H_5$ (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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Relative reactivity of ...

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then the α-compounds and the γ-compounds in this order. By action of electrophilic reagents another reactivity series of the compounds was observed: $\beta > \alpha$. This is also true for silico-olefines. In radical reactions the reactivity sequence of the compounds is $\alpha\,\gamma \gg \beta$. 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 $R_3SiCH_2CH = CH_2$ while the same addition to $Cl_3SiCH_2CH = CH_2$ 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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ASSOCIATION: Institut organicheskoy khimii AN SSSR, Moskva (Institute of Organic Chemistry of the AS USSR, Moscow)

Card 3/3

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FREYDLIN, L.Kh.; ZHUKOVA, I.F.; MIRONOV, V.F.

Effect of the structure of unsaturated organosilicon compounds on the rate of their hydrogenation. Izv. AN SSSR. Otd.khim.nauk no.7:1269-1274 Jl '61. (MIRA 14:7)

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

MIRONOV, V.F.; NEPOMNINA, V.V.

Rearrangement proceeding during the dehydochlorination of 1, 2-bis(trichlorosilyl) dichloroethanes by aluminum chloride. Izv.AN SSSR.Otd.khim.nauk no.10:1795-1799 O '61. (MIRA 14:10)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Silane) (Hydrochloric acid)

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B1_6/B1

AUTHORS: Mironov, V. F., and [illegible], V. V.

TITLE: Synthesis of alkenyl silanes by high-temperature [illegible] of unsaturated compounds with silicon hydrides

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye [illegible] nauk, no. 1_, 1961, 1_6 - [illegible]

TEXT: It was shown in previous papers (Ref. 1: V. F. Mironov, Author's Certificate 126653 (1960); Byul. izobr., No. [illegible], 19 (1960); Chem. Abstrs 54, 19485 (1960); Ref. 2: V. F. Mironov, [illegible] Chem. Commun. 25, 2167 (1960); Ref. 3: V. F. Mironov, A. D. Petrov, V. V. Pisarenko, Dokl. AN SSSR 124, 102 (1959)) that ethylene and propylene are converted into the corresponding alkenyl silanes when shortly heated to ~600°C together with silicon hydrides: $CH_2=CH_2 + HSiCl_3 \xrightarrow{600^\circ C} CH_2=CHSiCl_3$ ([illegible]%), $CH_3CH=CH_2 + HSiCl_3 \longrightarrow CH_2=CHCH_2SiCl_3 + CH_3CH=CHSiCl_3$ (10%). The authors used the new

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