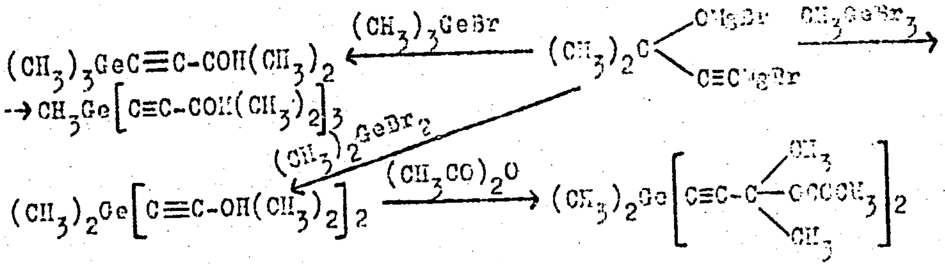
5 (3)

AUTHORS:	Shikhiyev, I. A., Shostakovskiy, M. F., Komarov, N. V. Aslanov, I. A.	SOV/79-29-5-31/75
TITLE:	Investigations in the Field of Synthesis and Transformations of Unsaturated Organo-germanium Compounds (Issledovaniya v oblasti sinteza i prevrashcheniy nepredel'nykh germaniyorganicheskikh soyedineniy). I. Synthesis of Mono-, Di-, and Trisubstituted Tertiary γ-Germanium Acetylene Alcohols (Sintez odno-, dvukh- i trekhatomnykh tretichnykh γ-germaniyatsetilenovykh spirtov)	
PERIODICAL:	Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1549-1551 (USSR)	
ABSTRACT:	In a previous paper (Ref 1) the reaction of di-magnesium-dibromodimethyl-ethinyl carbinol (Iotsich Reagent) with various alkyl-(aryl)-chlorosilanes was investigated. In order to explain further the reaction process with this reagent, its influence upon methyl-, dimethyl-, and trimethyl germanium bromides was investigated. The reaction was found to proceed with the formation of tertiary γ-germanium containing acetylene alcohols according to the following scheme:	

Card 1/3

Investigations in the Field of Synthesis and Transformations of Unsaturated Organo-germanium Compounds. I. Synthesis of Mono-, Di-, and Trisubstituted Tertiary γ-Germanium Acetylene Alcohols SOV/79-29-5-31/75



The occurrence of hydroxyl groups was confirmed by the acetic acid derivative of bis-(2-methylbutin-3-ol-2)-dimethyl germanium. Further reactions of organo-germanium alcohols and their derivatives will be described in later papers. The experimental part presents the physical data of the initial substances, the details of the synthesis, and the analysis of the compounds obtained. The authors prepared: (2-methyl-butin-3-ol-2)-4-trimethyl germanium, bis-(2-methyl-butin-3-ol-2)-4-dimethyl germanium, tri-(2-methyl-butin-3-ol-2)-4-methyl germanium, and bis-(2-methyl-butine-3-acetoxy-2)-4-dimethyl germanium, and

Investigations in the Field of Synthesis and SOV/79-29-5-31/75
Transformations of Unsaturated Organo-germanium Compounds. I. Synthesis of Mono-, Di-, and Trisubstituted Tertiary γ-Germanium Acetylene Alcohols

germanium. There are 3 Soviet references.

SUBMITTED: November 25, 1957

Card 3/3

KOMAROV, N.V.

PHASE I BOOK EXPLOITATION SOV/4989

Shikhiyev, Ibragim Abasovich, Professor, Doctor of Chemical Sciences, Mikhail Fedorovich Shostakovskiy, Professor, Doctor of Chemical Sciences, Nikolay Vasil'yevich Komarov, Candidate of Chemical Sciences

Novyye, kislorodsoderzhashchiye kremneorganicheskiye soyedineniyya (New Oxygen-Containing Silicon Organic Compounds) Baku, Azerneftneshr, 1960. 190 p. Errata slip inserted. 1,000 copies printed.

Ed. (Title page): Yu. G. Mamedaliyev, Academician of the Academy of Sciences Azerbaydzhanskaya SSR, Professor; Ed. of Publishing House: A. S. Shteyngel'.

PURPOSE: This book is intended for persons working with organosilicon compounds, and for students in schools of higher education.

COVERAGE: The book deals with the chemistry of organosilicon compounds, including their synthesis and conversion. It describes the use of organosilicon compounds in the manufacture of heat-resistant and electric insulating materials, anticorrosive

Card 1/7

Card 2/7

SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.; KOMAROV, N.V.

A.E. Favorskii; on the centennial of his birth. Azerb.khim. zhur. no.2:69-73 '60. (MIRA 14:8)
(Favorskii, Aleksei Efgrafovich, 1860-1945)

05000

S/062/60/000/007/016/017/XX
B004/B064

5.3700 2209, 1153, 1273

AUTHORS: Komarov, N. V., and Shostakovskiy, M. F.

TITLE: Synthesis of Primary γ-Organo Silicon Acetylene Alcohols

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 7, pp. 1300 - 1302

TEXT: The authors studied the synthesis of acetylene alcohols containing silicon or germanium (Refs. 1 - 3). In this paper, they report on the synthesis of primary γ-organo silicon acetylene alcohols. The reaction proceeded according to the following equation:

$R_3SiCl + BrMgC{\equiv}C-CH_2OMgBr \longrightarrow R_3SiC{\equiv}C-CH_2OH$; (R= alkyl or aryl).

The structure of the alcohols was confirmed by hydrogenation or acetalization. The authors describe: 1) The synthesis of 3-trimethyl silyl propin-2-ol-1 (A); $(CH_3)_3SiC{\equiv}C-CH_2OH$ in the water bath by means of ethyl magnesium bromide in etheric solution, dropwise addition of propargyl alcohol and, finally, addition of $CuCl_2$ and trimethyl chloro

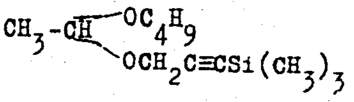
Card 1/3

05666

Synthesis of Primary γ-Organo Silicon Acetylene Alcohols

S/062/60/000/007/016/017/XX
B004/B064

silane. After cooling down the reaction mixture is diluted with ether, 5% HCl is added, and the compound extracted with ether; the yield is 40.2%. 3-triethyl silyl propin-2-ol-1 and dimethyl phenyl silyl propin-2-ol-1 were synthesized in the same way. 2) The synthesis of 3-trimethyl silyl propine-2-butyl acetal



$$CH_3-\underline{CH}\begin{matrix} \diagup OC_4H_9 \\ \diagdown OCH_2C{\equiv}CSi(CH_3)_3 \end{matrix}$$

originated from a mixture of vinyl butyl ether and compound A to which 1 drop of concentrated HCl was added. Then the substance was heated to 79°C. Vacuum distillation is carried out after neutralization with anhydrous potash; the yield is 71%. 3) 3-trimethyl silyl propanol-1, whose physical data are in agreement with the published ones, was obtained from A by hydrogenation in ethanolic solution on the Raney nickel catalyst. There are 1 table and 5 Soviet references.

Card 2/3

85666

Synthesis of Primary γ-Organo
Silicon Acetylene Alcohols

S/062/60/000/007/016/017/XX
B004/B064

ASSOCIATION: Irkutskiy institut organicheskoy khimii, Vostochno-Sibirskiy filial Sibirskogo otdeleniya Akademii nauk SSSR (Irkutsk Institute of Organic Chemistry, Eastern Siberian Branch of the Siberian Department of the Academy of Sciences USSR)

SUBMITTED: December 15, 1959

Card 3/3

22517

S/062/61/000/004/006/008
B118/B208

5.3700 2209

AUTHORS: Shostakovskiy, M. F., Komarov, N. V., Kuznetsova, V. P., and Igonina, I. I.

TITLE: Study in the field of synthesis and conversions of unsaturated organosilicon compounds. 1. Esterification of primary and tertiary γ-silicon-containing acetylene alcohols by adipic acid

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, no. 4, 1961, 699-703

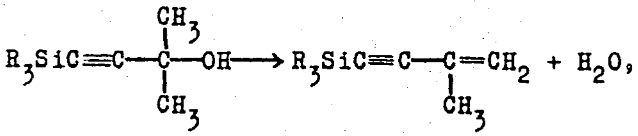
TEXT: The authors studied the esterification of primary and tertiary γ-silicon-containing acetylene alcohols with adipic acid. This esterification was accomplished by direct reaction of the alcohols with adipic acid, and by reaction of these alcohols, or their magnesium derivatives, with adipic acid chloride. The esterification of the primary γ-silicon-containing acetylene alcohols with adipic acid without catalysts takes place either to form the acid adipic ester: $R_3SiC\equiv C-CH_2OH + HOOC(CH_2)_4COOH \rightarrow R_3SiC\equiv C-CH_2OOC(CH_2)_4COOH$, where

Card 1/4

R = CH_3, C_2H_5, and C_6H_5, or to form the neutral adipic ester:

$$2R_3SiC{\equiv}C\text{-}CH_2OH + HOOC(CH_2)_4COOH \rightarrow R_3SiC{\equiv}C\text{-}CH_2OOC(CH_2)_4COOCH_2C{\equiv}CSiR_3,$$

where R = CH_3 and C_6H_5, depending on the conditions and the quantitative ratio of the components. This method is, however, not applicable to the esterification of tertiary γ-silicon-containing acetylene alcohols, since the reaction of these alcohols with adipic acid, with or without acid catalysts (such as boric acid etc.) gives rise to dehydration of the initial alcohols with formation of the corresponding silicon vinyl acetylene hydrocarbons:



$$R_3SiC{\equiv}C\text{—}\underset{CH_3}{\overset{CH_3}{C}}\text{—}OH \longrightarrow R_3SiC{\equiv}C\text{—}\underset{CH_3}{C}{=}CH_2 + H_2O,$$

where R = CH_3 and C_2H_5. Also the esterification of tertiary γ-silicon-containing acetylene alcohols by their reaction with adipic acid chloride in the presence of pyridine as well as the ester interchange of these alcohols with dimethyl adipate under the action of sodium ethylate were unsuccessful. The synthesis of

22517

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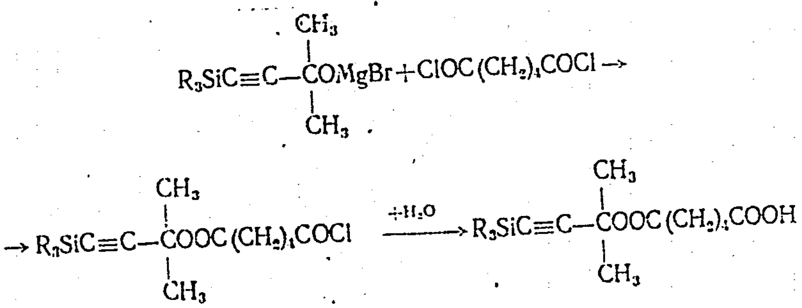
Study in the field...

acid and neutral esters of tertiary γ-silicon-containing acetylene alcohols was accomplished by reaction of magnesium alcoholates with adipic acid chloride



$$R_3SiC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}OMgBr+ClOC(CH_2)_4COCl\rightarrow$$

$$\rightarrow R_3SiC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}OOC(CH_2)_4COCl\xrightarrow{+H_2O}R_3SiC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}OOC(CH_2)_4COOH$$

Card 3/4

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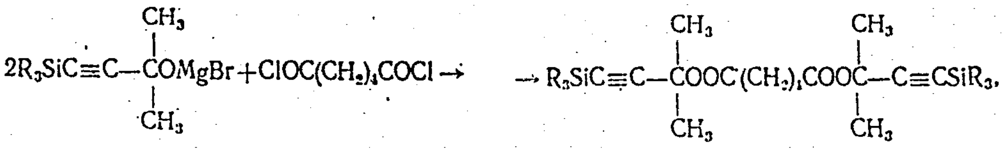
Study in the field...



$$2R_3SiC{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{C}}OMgBr + ClOC(CH_2)_4COCl \rightarrow R_3SiC{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{C}}OOC(CH_2)_4COO\overset{CH_3}{\underset{CH_3}{C}}{-}C{\equiv}CSiR_3,$$

где $R = CH_3$ и C_2H_5.

There are 7 Soviet-bloc references.

ASSOCIATION: Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR (Irkutsk Institute of Organic Chemistry of the Siberian Branch of the Academy of Sciences USSR)

SUBMITTED: December 15, 1959

Card 4/4

22518

S/062/61/000/004/007/008
B118/B208

5.3700 2209

AUTHORS: Shostakovskiy, M. F., Kaliberdo, L. M., and Komarov, N. V.

TITLE: Studies in the field of synthesis and conversions of unsaturated organosilicon compounds. 2. Cyanoethylation of tertiary γ-silicon-containing acetylene alcohols

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, no. 4, 1961, 703-705

TEXT: Cyanoethylation of secondary and tertiary silicon-containing alcohols has as yet not been described, unlike that of the primary ones. There are also no data available on the reaction of acrylonitrile with silicon-containing acetylene alcohols, in spite of the considerable importance of the cyanoethylation of acetylene alcohols and glycols. The authors therefore studied the cyanoethylation of tertiary γ-silicon-containing acetylene alcohols:

Card 1/3

22518

Studies in the field...

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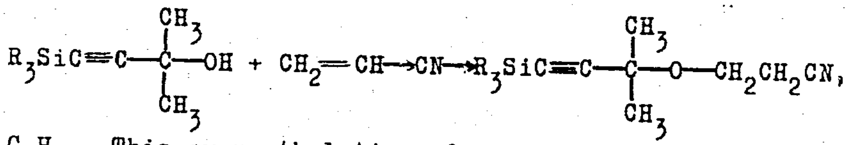
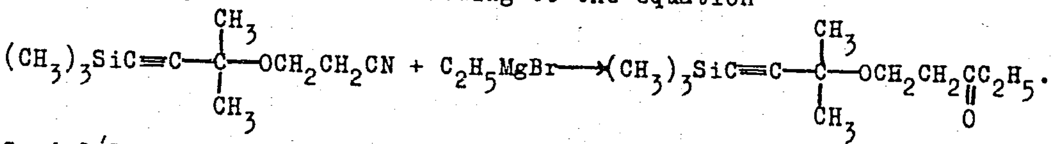


$$R_3SiC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-OH + CH_2=CH-CN\rightarrow R_3SiC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_2CH_2CN,$$

where R = CH_3 and C_2H_5. This cyanoethylation of acetylene alcohols was carried out under the action of a 40% aqueous caustic potash solution and also of sodium methylate. The catalytic effect of caustic potash solution gave no β-cyanoethyl ethers. The application of sodium methylate permitted the synthesis of β-cyanoethyl ethers of the silicon-containing acetylene alcohols used (50-60% yields). The reaction is exothermic. Better yields are obtained by using benzene as the solvent. The reaction of the β-cyanoethyl ether of 4-trimethyl-silyl-2-methyl butyn-3-ol-2 with ethyl magnesium bromide gave, like several analogous cases, the corresponding silicon acetylene ketone according to the equation



$$(CH_3)_3SiC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-OCH_2CH_2CN + C_2H_5MgBr\rightarrow(CH_3)_3SiC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-OCH_2CH_2\underset{O}{\underset{\|}{C}}C_2H_5.$$

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Card 2/3

22518

S/062/61/000/004/007/008
B118/B208

Studies in the field...

presence of a carbonyl group in this compound was confirmed by the formation of 2,4-dinitro-phenyl hydrazone. In addition to the formation of the organosilicon ketone according to this equation also a cleavage of the β-cyanoethyl ether takes place to give 4-trimethyl-silyl-2-methyl-butyn-3-ol-2. Other conversions of the β-cyanoethyl ethers of tertiary γ-silicon-containing acetylene alcohols will be described in the following report. There are 8 references: 4 Soviet-bloc and 4 non-Soviet-bloc. The two references to English-language publications read as follows: R. Cookson, F. Mann, J. Chem. Soc. 618 (1947), 67 (1949); S. Nozakura, S. Konotsune, Bull. Chim. Soc. Japan 29, 322, 326 (1956).

ASSOCIATION: Institut khimii Vostochno-Sibirskogo filiala Sibirskogo otdeleniya AN SSSR (Institute of Chemistry of the Eastern Siberian Branch of the Siberian Department, Academy of Sciences USSR)

SUBMITTED: December 15, 1959

Card 3/3

24421
S/079/61/031/007/003/008
D229/D305

5.3700

AUTHORS: Komarov, N.V., Shostakovskiy, M.F., and Astaf'yeva, L.N.

TITLE: Interaction of γ-silicon acetylenic alcohols with thionyl chloride

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 7, 1961, 2100 - 2102

TEXT: This is a report on the syntheses and properties of new silico-organic compounds. The present work is a continuation of an earlier investigation concerning the syntheses and substitution reactions of numerous acetylenic alcohols containing inorganic elements. It was found in this work that γ-silicon acetylenic alcohols reacted with thionyl chloride to form corresponding chlorides:

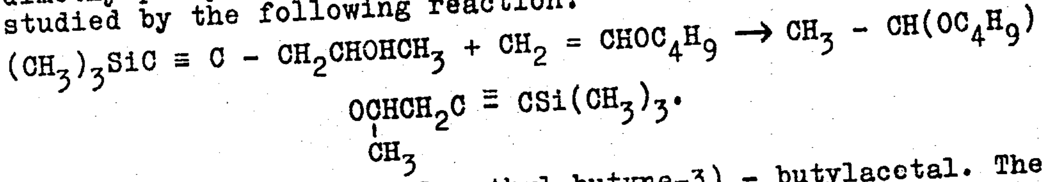
$$R_3SiC \equiv C - CH_2OH + SOCl_2 \longrightarrow R_3SiC \equiv C - CH_2Cl + HCl + SO_2,$$

Card 1/4

Interaction of γ-silicon ...

$R = CH_3, C_2H_5, C_6H_5.$

Thus, new compounds were synthesized: 3-chloropropyne-1 - trimethylsilane, 3-chloropropyne-1-triethylsilane and 3-chloropropyne-1-dimethylphenylsilane. The reactivity of the above chlorides was studied by the following reaction:



$$(CH_3)_3SiC \equiv C - CH_2CHOHCH_3 + CH_2 = CHOC_4H_9 \rightarrow CH_3 - CH(OC_4H_9)\underset{\substack{| \\ CH_3}}{OCH}CH_2C \equiv CSi(CH_3)_3.$$

named (4-trimethylsilyl-1-methyl-butyne-3) - butylacetal. The synthesis of $(CH_3)_3$ SiC C-CH_2Cl, designated 3-chloropropyne-1-trimethylsilane is then described. Characteristics of the product are: b.p. $50^0/17$ mm, n_D^{20} 1.4546, d_4^{20} 0.9295, MR_D 42.87; calc. 42.77 [Abstractor's note: MR_D not defined]. Found percent: Si 18.84, $C_6H_{11}SiCl$. Calculated percent: Si 19.14. The synthesis of $(C_2H_5)_3$ SiC C-

24421

S/079/61/031/007/003/008
D229/D305

Interaction of γ-silicon ...

CH_2Cl, named 3-chloropropyne-1-triethylsilane, was analogous to that of 3-chloropropyne-1-trimethylsilane. Quantities used: 8.92 gr. of thionyl chloride, 1gr. of pyridine, 9.51 gr. of 3-triethylsilylpropyne-2-ol-1 (b.p. 109-110°/6 mm, n_D^{20} 1.4670, d_4^{20} 0.8932). The yield was 8.95 gr. (95 %). Characteristics of products b.p. 72°/6 mm, n_D^{20} 1.4698, d_4^{20} 0.9262, MR_D 57.03: calculated 56.66. Found percent: Si 15.16. C_9H_{17} SiCl. Calculated percent Si 14.84. Synthesis of $(CH_3)_2 - \underset{C_6H_5}{Si}C \equiv C-CH_2Cl$ named 3-chloropropyne-1-dimethylphenylsilane was analogous to that of 3-chloropropyne-1-trimethylsilane. Characteristics of product: b.p. 118°/6 mm, n_D^{20} 1.5345, MR_C 62.39; calculated 62.44. Found percent: Si 13.54. $C_{11}H_{13}$ SiCl. Calculated percent: Si 13.42. The authors then describe the synthesis of 5-tri-

Card 3/4

methylsilypentyne-4-ol-2. The yield was 3.5 gr. (16.4 %). The characteristics of the product: b.p. 95-97°/2 mm, n_D^{20} 1.4748, d_4^{20} 0.9101. Found MR_D 48.46: calculated 48.74. Found percent: Si 17.90 $C_8H_{16}OSi$. Calculated percent Si 17.9. Finally the synthesis of 4-trimethylsilyl-1-methylbutyne-3/butylacetyl is examined. The yield was 4.68 gr. (97.5 %). Characteristics of the product: b.p. 153°/3 mm, n_D^{20} 1.4655, d_4^{20} 0.8925, MR_D^2 79.12; calculated 78.51. Found percent: Si 11.52. $C_{14}H_{26}\ O_2Si$. Calculated percent: Si 11.00. There are 2 Soviet-bloc references.

ASSOCIATION: Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya akademii nauk SSSR (Irkutsk Institute of Organic Chemistry, Siberian Division, Academy of Sciences USSR)

SUBMITTED: July 27, 1960

SHOSTAKOVSKIY, M.F.; KALABINA, A.V.; KOMAROV, N.V.

Synthesis and transformations of vinyl aryl ethers. Report No.1: Synthesis and properties of vinyl ether of p-sec-propylphenol. Izv. Fiz.-khim. nauch.-issl. inst. Irk. un. 5 no.1:215-224 '61.
(MIRA 16:8)

(Ethers) (Phenol)

25365

S/079/61/031/008/003/009
D215/D304

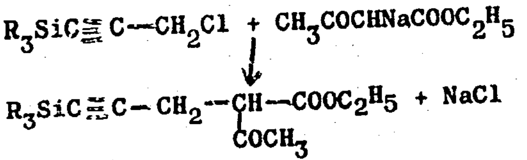
5 3700

AUTHORS: Shostakovskiy, M.F., Kuznetsova, V.P., and Komarov, N.V.

TITLE: Study of synthesis and transformations of unsaturated organo-silicon compounds: interaction of γ-silicon-acetylene chlorides with sodium-acetoacetic and sodium-malonic esters

PERIODICAL: Zhurnal obshchey khimii, 1961, v. 31, no. 8, 2504-2507

TEXT: This paper studies reactions of γ-Si-acetylene chlorides of the propargyl type with Na acetoacetic and Na malonic esters and the prospects of obtaining Si-acetylene carbonyl compounds from these reactions. The reaction is smooth and the yield of keto-esters reaches 40-50%:



$$R_3SiC\equiv C-CH_2Cl + CH_3COCHNaCOOC_2H_5 \longrightarrow R_3SiC\equiv C-CH_2-\underset{COCH_3}{CH}-COOC_2H_5 + NaCl$$

(R is CH_3, C_2H_5 or C_6H_5)

Card 1/3

25365

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D215/D304

Study of synthesis...

A Si-acetylene acid was obtained by the following reaction -

$$(C_2H_5)_3SiC\equiv C-CH_2Cl + NaCH(COOC_2H_5)_2$$

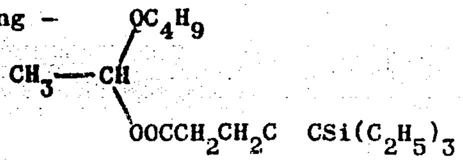
$$\downarrow$$

$$(C_2H_5)_3SiC\equiv CCH_2CH(COOC_2H_5)_2$$

$$\Big\downarrow{+H_2O}$$

$$(C_2H_5)_3SIC\equiv C-CH_2-CH_2-COOH + CO_2 + 2C_2H_5OH$$

The presence of the carboxyl group in the product of this reaction was established by reaction with vinylbutyl ester - forming -



$$CH_3-CH(OC_4H_9)(OOCCH_2CH_2C\equiv CSi(C_2H_5)_3)$$

Card 2/3

25365

S/079/61/031/008/003/009
D215/D304

Study of synthesis...

The acylal formed hydrolyzes to form the original Si-acetylene acid together with butyl alcohol and acetaldehyde. The stages in which the original Si-acetylebe keto-ester is converted into the acid are two, i.e. formation of a Si-acetylene keto-acid which then breaks down with fission of the $Si\equiv C$ bond. Synthesis of the following new compounds is described: 6-trimethylsilyl-3-carbetoxyhexene-5-on-2,6-trisethylsilyl-3-carbetoxyhexene-5-on-2;6-dimethylphenylsilyl-3-carbetoxyhexene-5-on-2,6-triethylsilyl-3-carboxyhexene,5-on-2,4-triethylsilyl-1-carboxybutene-3, 1-butoxyethyl ester (4-triethylsilyl-1-carboxybutene-3). There are 3 Soviet-bloc references.

ASSOCIATION: Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya akademiy nauk SSSR (Irkutsk Institute of Organic Chemistry, Siberian Division, Academy of Sciences, USSR)

SUBMITTED: July 25, 1960

Card 3/3

88407

5.3700

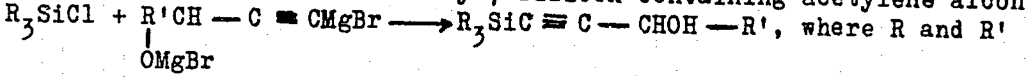
S/020/61/136/004/016/026
B016/B075

AUTHORS: Shostakovskiy, M. F., Corresponding Member AS USSR, Komarov, N. V., and Pukhnarevich, V. B.

TITLE: Synthesis and Some Conversions of Secondary γ-Silicon-containing Acetylene Alcohols

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 4, pp. 846-848

TEXT: Proceeding from the reaction of chlorosilanes with dimagnesium bromine derivatives of secondary acetylene alcohols the authors elaborated a synthesis method of secondary γ-silicon-containing acetylene alcohols:



$R_3SiCl + \underset{\substack{| \\ OMgBr}}{R'CH} - C \equiv CMgBr \rightarrow R_3SiC \equiv C - CHOH - R'$, where R and R'

denote CH_3, C_2H_5, and other organic radicals. Furthermore, the reaction of the synthesized alcohols has been studied 1) with thionyl chloride

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88407

Synthesis and Some Conversions of Secondary γ-Silicon-containing Acetylene Alcohols

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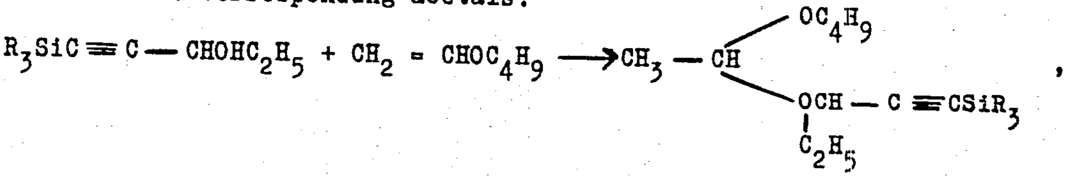
B016/B075

and 2) with vinyl ethers. To 1): Substitution of hydroxyl by a chlorine atom proceeds under relatively mild conditions and results in the corresponding siliconacetylene chlorides. The Si-C bond is not ruptured. $R_3SiC \equiv C - CHOHC_2H_5 + SOCl_2 \rightarrow R_3SiC \equiv C - CHClC_2H_5 + SO_2 + HCl$, where $R = CH_3$ and C_2H_5. To 2): Reaction with vinyl ethers proceeds easily and leads to the corresponding acetals:



$$R_3SiC \equiv C - CHOHC_2H_5 + CH_2 = CHOC_4H_9 \rightarrow CH_3 - CH\left\langle \begin{array}{l} OC_4H_9 \\ \underset{\substack{| \\ C_2H_5}}{OCH} - C \equiv CSiR_3 \end{array}\right. ,$$

where $R = CH_3$ and C_2H_5. The following compounds were synthesized according to (1): 5-trimethyl-silyl-pentin-4-ol-3, 5-triethyl-silyl-pentin-4-ol-3, 3-chloro 5-trimethyl-silyl-pentine-4, and 3-chloro 5-triethyl-silyl-pentine-4; reaction 2 led to: butyl-(3-trimethyl-silyl-

88407

Synthesis and Some Conversions of Secondary
γ-Silicon-containing Acetylene Alcohols

S/020/61/136/004/016/026
B016/B075

1-ethyl-propine-2)-acetal and butyl-(3-triethyl-silyl-1-ethyl-propine-2)-acetal. There are 3 Soviet references.

ASSOCIATION: Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya Akademii nauk SSSR (Irkutsk Institute of Organic Chemistry of the Siberian Branch, Academy of Sciences USSR)

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SUBMITTED: October 12, 1960

Card 3/3

SHOSTAKOVSKIY, M.F.; KOMAROV, N.V.; MAROSHIN, Yu.V.

Synthesis and some transformations of silanols in the vinylacetylene series. Dokl. AN SSSR 139 no.4:913-915 Ag '61. (MIRA 14:7)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR. 2. Chlen-korrespondent AN SSSR (for Shostakovskiy).
(Silanol)

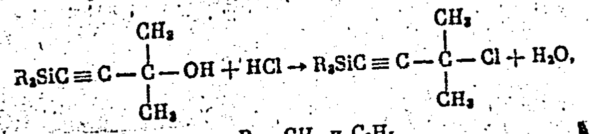
S/062/62/000/003/013/014
B110/B101

AUTHORS: Shostakovskiy, M. F., Komarov, N. V., Kuznetsova, V. P., and Igonina, I. I.

TITLE: Investigations into synthesis and conversions of unsaturated organosilicon compounds. Communication 3. Interaction of tertiary γ-silicon acetylene alcohols with concentrated hydrochloric acid and thionyl chloride

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 3, 1962, 510-512

TEXT: The reaction of tertiary γ-silicon acetylene alcohols with concentrated hydrochloric acid and thionyl chloride showed that the low homologs of tertiary γ-silicon acetylene compounds react easily and almost quantitatively with concentrated hydrochloric acid:

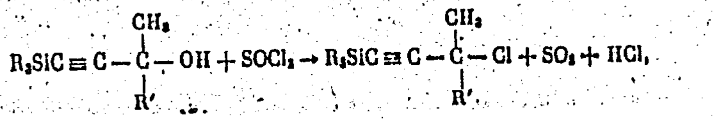


$$R_3SiC\equiv C-\underset{CH_3}{\overset{CH_3}{C}}-OH+HCl\rightarrow R_3SiC\equiv C-\underset{CH_3}{\overset{CH_3}{C}}-Cl+H_2O, \qquad (1)$$

where $R = CH_3$ и C_2H_5.

Card 1/3

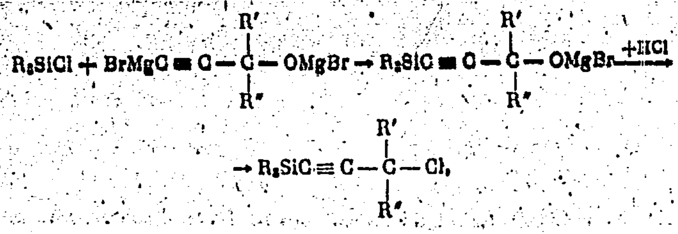
Rupture of the Si-C bond conjugated with the triple bond does not take place here. The exchange of hydroxyl for chlorine only occurs partially; it could be obtained, however, with $SOCl_2$;



$$R_3SiC\equiv C-\overset{CH_3}{\underset{R'}{C}}-OH+SOCl_2\rightarrow R_3SiC\equiv C-\overset{CH_3}{\underset{R'}{C}}-Cl+SO_2+HCl, \quad (2)$$

where R and R' = CH_3, C_2H_5 etc.

Here too, the Si-C bond is stable. Tertiary γ-silicon acetylene chlorides may be obtained directly from triaryl(alkyl)chlorosilanes, magnesium derivatives of acetylene alcohols and concentrated HCl:



$$R_3SiCl+BrMgC\equiv C-\overset{R'}{\underset{R''}{C}}-OMgBr\rightarrow R_3SiC\equiv C-\overset{R'}{\underset{R''}{C}}-OMgBr\xrightarrow{+HCl}$$
$$\rightarrow R_3SiC\equiv C-\overset{R'}{\underset{R''}{C}}-Cl, \quad (3)$$

Card 2/3

where R, R' and R" are organic radicals. This method produces a 70 % yield. Tertiary γ-silicon acetylene chlorides are colorless, easily movable liquids of specific odor, soluble in organic solvents and insoluble in water. The following compounds were synthesized from the corresponding alcohols: 4-trimethyl-silyl-2-methyl-2-chlorobutyne-3, b.49°C (14 mm Hg), n_D^{20} 1.4415, d_4^{20} 0.8774; 5-trimethyl-silyl-3-methyl-3-chloropentyne-4, b.61-62°C (8 mm Hg), n_D^{20} 1.4602, d_4^{20} 0.9082, and 4-triethyl-silyl-2-methyl-2-chlorobutyne-3, b.101-102°C. (16 mm Hg), n_D^{20} 1.4525, d_4^{20} 0.8861.

ASSOCIATION: Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya Akademii nauk SSSR (Irkutsk Institute of Organic Chemistry of the Siberian Department of the Academy of Sciences USSR)

SUBMITTED: October 24, 1961

Card 3/3

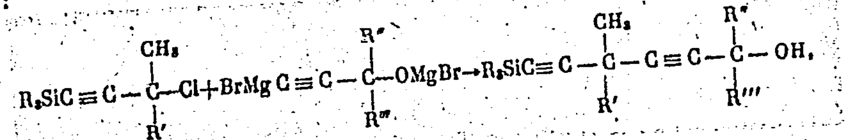
S/062/62/000/003/014/014
B110/B101

AUTHORS: Shostakovskiy, M. F., Komarov, N. V., Kuznetsova, V. P., Igonina, I. I., and Semenova, N. V.

TITLE: Investigations into synthesis and conversions of unsaturated organosilicon compounds. Communication 4. Synthesis and some conversions of organosilicon diacetylene alcohols with isolated ternary bonds

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 3, 1962, 512-515

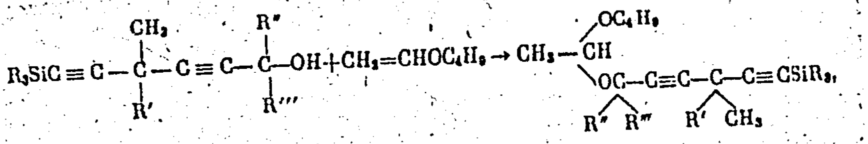
TEXT: The reaction of tertiary γ-silicon acetylene chlorides with magnesium derivatives of primary, secondary and tertiary acetylene alcohols was studied:



$$R_3SiC\equiv C-\underset{R'}{\overset{CH_3}{C}}-Cl+BrMgC\equiv C-\underset{R'''}{\overset{R''}{C}}-OMgBr\rightarrow R_3SiC\equiv C-\underset{R'}{\overset{CH_3}{C}}-C\equiv C-\underset{R'''}{\overset{R''}{C}}-OH,$$

---

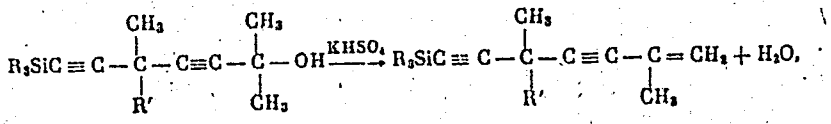
where R and R' are similar or dissimilar organic radicals, R" and R"' = H or organic radicals. The reaction proceeds easily under formation of organosilicon diacetylene compounds with isolated ternary bonds. The behavior of this new class of organosilicon compounds was tested with regard to acetal formation, dehydration and exchange of hydroxyl for halogen. Organosilicon diacetylene alcohols with vinyl butyl ether produced organosilicon diacetylene acetals, not yet described:



where R and R' are similar and dissimilar organic radicals; R" and R"' = H or organic radicals. Primary alcohols react without catalyst under heating, secondary ones without catalyst during heating, and tertiary ones require concentrated hydrochloric acid as catalyst. Tertiary silicon acetylene alcohols are dehydrated by the action of $KHSO_4$:

S/062/62/000/003/014/014
B110/B101

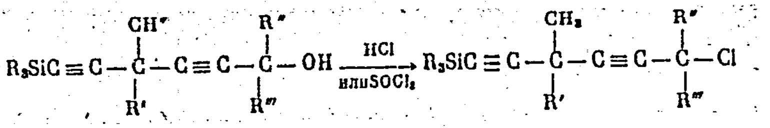
Investigations into synthesis and...



$$R_3SiC\equiv C-\underset{R'}{\overset{CH_3}{C}}-C\equiv C-\underset{CH_3}{\overset{CH_3}{C}}-OH\xrightarrow{KHSO_4}R_3SiC\equiv C-\underset{R'}{\overset{CH_3}{C}}-C\equiv C-\underset{CH_3}{C}=CH_2+H_2O,$$

where $R = CH_3$; $R' = CH_3$ и C_2H_5.

The dehydration of secondary alcohols is not possible in this way. When treated with concentrated hydrochloric acid or thionyl chloride, tertiary alcohols exchange hydroxyl for chlorine:



$$R_3SiC\equiv C-\underset{R'}{\overset{CH_3}{C}}-C\equiv C-\underset{R'''}{\overset{R''}{C}}-OH\xrightarrow[\text{или }SOCl_2]{HCl}R_3SiC\equiv C-\underset{R'}{\overset{CH_3}{C}}-C\equiv C-\underset{R'''}{\overset{R''}{C}}-Cl$$

no rupture taking place at the Si-C bond conjugated to the triple bond. The following compounds were synthesized: 6-trimetyhl-silyl-4,4-dimethyl-hexadiin-2,5-ol-1, b.98-99°C (2 mm Hg), n_D^{20} 1.4736, d_4^{20} 0.8973; 7-trimethyl-silyl-5,5-dimethyl-heptadiin-3,6-ol-2, b.116°C (12 mm Hg),

Card 3/5

n_D^{20} 1.4675, d_4^{20} 0.8930; 7-trimethyl-silyl-2,5,5-trimethyl-heptadiin-3,6-ol-2, b.102°C (7 mm Hg), m.41-42°C; 7-trimethyl-silyl-2,5-dimethyl-5-ethyl-heptadiin-3,6-ol-2, b. 105°C (6 mm Hg), n_D^{20} 1.4697, d_4^{20} 0.8867; 6-trimethyl-silyl-4,4-dimethyl-hexadiin-2,5-butylacetal, b.133-134°C (5 mm Hg), n_D^{20} 1.4590, d_4^{20} 0.8993; 6-trimethyl-silyl-1,4,4-trimethyl-hexadiin-2,5-butylacetal, b.121-122°C (2 mm Hg), n_D^{20} 1.4465, d_4^{20} 0.8670; 6-trimethyl-silyl-1,1,4,4-tetramethyl-hexadiin-2,5-butylacetal, b.134-135°C (9 mm Hg), n_D^{20} 1.4439, d_4^{20} 0.8523; 6-trimethyl-silyl-1,1,4-trimethyl-4-ethylhexadiin-2,5-butylacetal, b.122-123°C (2 mm Hg), n_D^{20} 1.4502, d_4^{20} 0.8786; 7-trimethyl-silyl-2,5,5-trimethyl-heptadiin-3,6-ene-1, b.90-91°C (7 mm Hg), n_D^{20} 1.4658, d_4^{20} 0.8187; 7-trimethyl-silyl-2,5-dimethyl-5-ethyl-heptadiin-3,6-ene-1, b.89-90°C (6 mm Hg), n_D^{20} 1.4732, d_4^{20} 0.8754; 7-trimethyl-silyl-2-chloro-2,5,5-trimethyl-heptadiin-3,6, b.78-79°C (3 mm Hg), n_D^{20} 1.4605, d_4^{20} 0.9044, and 7-trimethyl-silyl-2-chloro-2,5-dimethyl-5-ethylheptadiin-3,6, b.93-94°C, n_D^{20} 1.4666, d_4^{20} 0.8982.

ASSOCIATION: Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya Akademii nauk SSSR (Irkutsk Institute of Organic Chemistry of the Siberian Branch of the Academy of Sciences USSR)

SUBMITTED: October 24, 1961

Card 5/5

33935
S/079/62/032/001/013/016
D204/D302

5.3700

AUTHORS: Shostakovskiy, M.F., and Komarov, N.V.

TITLE: The interaction of polyorganosiloxanes with Iositch reagents

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 1, 1962, 320-321

TEXT: A study of the interaction of polyorganosiloxanes with Iositch reagents [Abstractor's note: Name transliterated], leading to the formation of acetylenic silanols, e.g.

$$(R_2SiO)_x + BrMgC \equiv CH \rightarrow HC \equiv CSiR_2OH$$

$$(R_2SiO)_x + BrMgC \equiv CMgBr \rightarrow HOR_2SiC \equiv CSiR_2OH$$

$$(R_2SiO)_x + BrMgC \equiv C - R' \rightarrow R'C \equiv CSiR_2OH$$

where R, R' are organic radicals and x is a whole number. The compounds dimethyl ethynyl silanol, 1,2-bis (dimethyl hydroxy silyl) acetylene, (3-methyl-butyn-1-01-3)-dimethyl silanol and diethyl vi-

Card 1/2

40732

5.3700

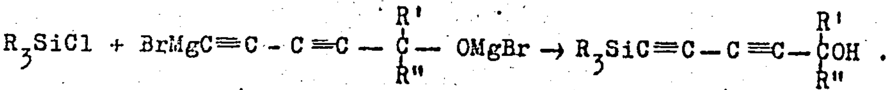
S/062/62/000/009/009/009
B119/B186

AUTHORS: Komarov, N. V., and Semenova, N. V.

TITLE: Synthesis of organosilicon diacetylene alcohols with conjugate triple bonds

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 9, 1962, 1694

TEXT: 6-trimethyl silyl-2-methyl hexadiin-3,5-ol-2 (I) was synthesized from 2-methyl hexadiin-3,5-ol-2 (II) and trimethyl chlorosilane. Also 6-dimethyl ethyl silyl-2-methyl hexadiin-3,5-ol-2 (III) was synthesized from II and dimethyl ethyl chlorosilane. **Both these reactions** correspond to the scheme:



$$R_3SiCl + BrMgC{\equiv}C-C{\equiv}C-\overset{R'}{\underset{R''}{C}}-OMgBr \rightarrow R_3SiC{\equiv}C-C{\equiv}C-\overset{R'}{\underset{R''}{C}}OH .$$

Yields were 68 % of I, and 56.5 % of III. I is white, silky-crystalline, odorless (after storing it takes a moldy odor), well soluble in organic solvents, insoluble in water; melting point 67°C, boiling point 85°C (at

Card 1/2

S/062/62/000/009/009/009
B119/B186

Synthesis of organosilicon ....

3 mm Hg). Properties of III: melting point 38°C, boiling point 110°C (at 4 mm Hg), n_D^{20} 1.4900, d_4^{20} 0.8874.

K

ASSOCIATION: Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR (Irkutsk Institute of Organic Chemistry of the Siberian Department AS USSR)

SUBMITTED: April 13, 1962

Card 2/2

SHOSTAKOVSKIY, M.F.; KOMAROV, N.V.; MISYUNAS, V.K.

Reaction of stannols with the Grignard reagent. Izv. AN SSSR [redacted].nauk no.2:368 F '62. (MIRA 15:2)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

(Tin organic compounds)
(Grignard reagents)

SHOSTAKOVSKIY, M.F.; KOMAROV, N.V.; KUZNETSOVA, V.P.; IGONINA, I.I.

Synthesis and transformations of unsaturated organosilicon compounds. Report No.3: Interaction of tertiary γ-siliconacetylenic alcohols with concentrated hydrochloric acid and thionyl chloride. Izv.AN SSSR.Otd.khim.nauk no.3:510-512 Mr '62. (MIRA 15:3)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.
(Silicon organic compounds) (Hydrochloric acid)
(Thionyl chloride)

SHOSTAKOVSKIY, M.F.; KOMAROV, N.V.; PUKHNAREVICH, V.B.; SKLYANOVA, A.M.

Synthesis and transformations of unsaturated organosilicon compounds. Report No.5: Synthesis and some transformations of 4-trimethylsilyl- and 4-triethylsilyl-3-butyn-2-ols. Izv.AN SSSR.Otd.khim.nauk no.6:1019-1024 '62. (MIRA 15:8)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya Akademii nauk SSSR.

(Silicon organic compounds) (Unsaturated compounds)

KOMAROV, N.V.; SEMENOVA, N.V.

Synthesis of organosilicon diacetylenic alcohols having conjugated triple bonds. Izv.AN SSSR.Otd.khim.nauk no.9:1694 S '62. (MIRA 15:10)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

(Silicon organic compounds) (Acetylene compounds)

SHOSTAKOVSKIY, M.F.; KOMAROV, N.V.; KUZNETSOVA, V.P.; IGONINA, I.I.;
SEMENOVA, N.V.

Synthesis and transformations of unsaturated organosilicon compounds. Report No.4: Synthesis and some transformations of organosilicon diacetylenic alcohols having **isolated** triple bonds. Izv.AN SSSR.Otd.khim.nauk no.3:512-515 Mr '62.

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.
(Silicon organic compounds) (Unsaturated compounds)

KOMARDV, N. V.; VLASOVA, N. N.

Synthesis and transformations of unsaturated organosilicon compounds. Report No. 6: Synthesis and some transformations of organosilicon acetylenic mercaptans. Izv. AN SSSR. Otd. khim. nauk no.1:90-96 '63. (MIRA 16:1)

1. Irkutskiy institut organicheskoy khimii AN SSSR.

(Silicon organic compounds)
(Acetylene compounds)

KOMAROV, N. V.; MAROSHIN, Yu. V.; LEBEDEVA, A. D.; ASTAF'YEVA, L. N.

Oxygen-containing organosilicon compounds. Report No. 7: Acetylene and vinylacetylene silanols and their transformations. Izv. AN SSSR. Otd. khim. nauk no.1:97-105 '63.
(MIRA 16:1)

1. Irkutskiy institut organicheskoy khimii AN SSSR.

(Silanol) (Unsaturated compounds)

[illegible] EPF(c)/EWP(j)/T Pc-4 Pr-4 [illegible]

[illegible] NR AP4047790 S [illegible] /0153

AUTHOR: Shostakovskiy, M. F.; Komarov, N. V.; Atavin, A. S.; Yegorov, N. V.; Yarosh,

TITLE: Synthesis of trimethylsilylethynyl-alpha-furylcarbinol

[illegible] SSSR. Sibirskoye otdeleniye. Izvestiya [illegible] khimicheskikh nauk, no. 2,

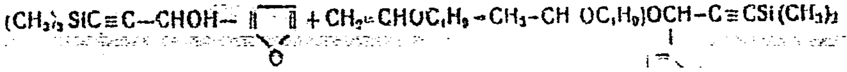
[illegible] organic compound, furane [illegible] derivative, acetylene, [illegible]

[illegible] authors studied the reactions [illegible] with a Mg- [illegible] furylethynylcarbinol, and 2) trime[illegible] magnesium bromide [illegible] smoothly realizable process [illegible] trimethylsilylethynyl-α- [illegible] according to the reaction

[illegible] MgBr [illegible] (1)

ACCESSION NR: AP4047790

pared butyl-(3-trimethylsilyl-1-α-furylpropargyl) acetal 128-130C/3.5 mm, the first representative of the silicoacetylene acetals with a heterocyclic substituent, by reacting trimethylsilylethynyl-α-furylcarbinol with vinyl butyl ether:



(2)

Methods for preparing the compounds are described and analytical results identifying them are presented. Orig. art. has: 3 formulas.

ASSOCIATION: Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR (Irkutsk Organic Chemistry Institute, Siberian branch, AN SSSR)

SUBMITTED: 11Mar64 ENCL: 00 SUB CODE: OC, GC

NO REF SOV: 002 OTHER: 001

ACCESSION NR: AP4019017 S/0062/64/000/002/0382/0384

AUTHORS: Shostakovskiy, M.F.; Komarova, L.I.; Pukhnarevich, V.B.; Komarov, N.V.; Roman, V.K.

TITLE: 3,5-dinitrobenzoylhydrazones of organo silicon carbonyl compounds

SOURCE: AN SSSR. Izv. Seriya khimicheskaya, no. 2, 1964, 382-384

TOPIC TAGS: dinitrobenzoyl hydrazone, dinitrobenzoyl hydrazide, organo silicon carbonyl reagent, hydrozone, carbonyl

ABSTRACT: In the search for a reagent able to identify organo silicon carbonyl compounds, the authors found that 3,5-dinitrobenzoylhydrazide readily forms good crystallizing 3,5-dinitrobenzoylhydrazones with organo silicon aldehydes and ketones. In this respect, the reagent is different from 2,4-dinitrophenylhydrazine, semi-carbazide and hydroxylamine. The tendency of organo silicon aldehydes and ketones to form these compounds and yields greatly depends on their structure. Thirteen compounds were investigated from this point of view and their behavior recorded in a comprehen-

Card 1/2

ACCESSION NR: AP4019017

sive table. The analytical method consists in dissolving approximately 0,001 M 3,5-dinitrobenzoylhydrazide in 10 ml ethanol, adding to it 0.0015 M silicoorganic carbonyl compound. The mixture is heated for half an hour to 50-60C and left standing to crystallize. Hydrazones so obtained are recrystallized from ethanol. They are white crystalline substances with a definite melting point and melt without decomposing. Orig. art. has: 3 formulas, 1 table.

ASSOCIATION: Irkutskiy institut organicheskoy khimii, AN SSSR (Irkutsk Institute of Organic Chemistry, AN SSSR)

SUBMITTED: 05Aug63 DATE ACQ: 27Mar64 ENCL: 00

SUB CODE: OC NR REF SOV: 001 OTHER: 000

Card 2/2

ACCESSION NR: AP4025012 S/0062/64/000/003/0565/0566

AUTHORS: Shostakovskiy, M.F.; Komarov, N.V.; Maroshin, Yu. V.;
Lebedeva, A. D.

TITLE: Synthesis of vinylacetylenic alkoxysilanes

SOURCE: AN SSSR. Izv. Seriya khimicheskaya, no. 3, 1964, 565-566

TOPIC TAGS: vinylacetylenic alkoxysilane, synthesis, vinylacetylenic chloride, continuous process

ABSTRACT: A method proposed for the synthesis of vinylacetylenealkoxysilanes (a new class of organosilicon compounds) includes the preparation of thedialkylvinylethynylbromomagnesiumalcoholate:

$$R'R''C=O + CH_2=CHC\equiv CMgBr \rightarrow R'R''(CH_2=CHC\equiv C)COMgBr$$

and reacting the latter with alkyl(aryl)chlorosilanes:

$$R'R''(CH_2=CHC\equiv C)COMgBr + R_3SiCl \rightarrow R_3SiOC(C\equiv CCH=CH_2)R'R''.$$

where R, R' and R" = H or organic radicals. The process may be continuous since the intermediate product does not need to be isolated.

ACCESSION NR: AP4025012

However, secondary reaction products are formed: vinylacetylene chlorides result from the reaction between the vinylacetylenealkoxysilane and the original chlorosilane under the influence of the magnesium halide:

$$R'R''(CH_2=CHC\equiv C)COSiR_3+R_3SiCl\rightarrow$$
$$\rightarrow R'R''(CH_2=CHC\equiv C)CCl+R_3SiOSiR_3$$

For instance, 1,1-dimethylpenten-4-yn-2-oxytrimethylsilane and trimethylchlorosilane reacted in the presence of 50% freshly prepared MgClBr to form the 1,1-dimethylpenten-4-yn-2,1-chloride. The (1,1-dimethylpenten-4-yn-2-oxy)trimethyl-, (1,1-dimethylpenten-4-yn-2-oxy)methylethyl- and (1-methyl-1-ethylpenten-4-yn-2-oxy)methylethyl-silanes were synthesized. These compounds are insoluble in water, soluble in organic solvents, unstable to acid, highly chemically reactive and polymerize on storage. Orig. art. has: 3 equations.

ASSOCIATION: Irkutskiy institut organicheskoy khimii Akademii nauk SSSR (Irkutsk Institute of Organic Chemistry, Academy of Sciences SSSR)

SUBMITTED: 07Aug63	DATE ACQ: 17Apr64	ENCL: 00
SUB CODE: CH	NR REF SOV: 006	OTHER: 001

Card 2/2

SHOSTAKOVSKIY, M.F.; KOMAROV, N.V.; MISYUNAS, V.K.; ZAINCHKOVSKAYA, M.K.

Nature of interaction between stannanol and the Iotsich reagent.
Izv. AN SSSR. Ser. khim. no.6:1102-1104 Je '64.
(MIRA 17:11)

1. Institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

SHOSTAKOVSKIY, M.F.; SHERGINA, N.N.; KOMAROV, N.V.; BRODSKAYA, E.I.;
IGONINA, I.I.

Vibrational spectra of some organosilicon acetylene and diacetylene compounds. Izv. AN SSSR. Ser. khim. no.6:1126-1128 Je '64. (MIRA 17:11)

1. Institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

EWT(m)/EPF(c)/EWP(j) Pc-4/Pr-4 AFMD(c)/AS(mp)-2/BSD/RAEM(a)/
SSD(c)/AFWL/ESD(gs)/ESD(t) RM

ACCESSION NR: AP4045798 S/0062/64/000/009/1606/1610

B

AUTHOR: **Shostakovskiy, M. F.; Shergina, N. I.; Komarov, N. V.; Maroshin,**

ion spectra of vinylacetylenic oxygen-containing organosilicon compounds

SSSR. Izv. Seriya khimicheskaya, no. 9, 1964, 1606-1610

vinylacetyleneorganosilane, vinylacetylenic organosiloxane, organosilanol, vibration spectrum, IR spectrum, Raman spectrum, group, vibration frequency, vibration intensity

The IR spectra and the Raman spectra of vinylacetylenic oxygen-organosilicon compounds were examined to determine if the oxygen groups COH, SiOH, COSi and SiOSi in the alpha-position with respect bond had any significant effect on the vibrations of the vinylace- Data was obtained for the following compounds: dimethylvinylethy- dimethylvinylethynylsilanol (II), dimethylvinylethynylmethoxytri- (III), pentamethylvinylethynyldisiloxane (IV), dimethylvinylethynyl-

L 18281-65
ACCESSION NR: AP4045798

[illegible] ...ethylsilane (V), bis(dimethylvinylethynylmethoxy)dimethylsilane [illegible] 1, 3-di(vinylethynyl)trisiloxane (VII), and tetramethyl-1, 2-di(vinylethynyl)disiloxane (VIII). The band characteristic of the acetylenic bond does not appear in the IR spectra of the vinylacetylenic alkoxysilanes V, V, VI, and [illegible] the analgous organosilicon compounds II, III, VII and VIII, the C≡C characterizing bands appear, at somewhat lower frequencies but higher intensi- [illegible] ...ylacetylenic hydrocarbons. On the other hand the vinylacetylene [illegible] little effect on the vibration frequency of the Si-OH, C-OH, Si-O-Si [illegible] ...nds. The values for the double bond frequencies characteristic [illegible] ... in all the compounds investigated and C-O-Si bonds. The values for the double bond frequencies characteristic group remained essentially constant in all the compounds investigated.

1 table and 1 figure

Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya
utsk Institute of Organic Chemistry Siberian Department AN SSSR)

29Dec62 ENCL: 00
GC NO REF SOV: 010 OTHER: 001

SHOSTAKOVSKIY, M.F.; KOMAROV, N.V.; GUSEVA, I.S.; MISYUNAS, V.K.

Interaction between stannanols and acetylenes. Dokl. AN SSSR 158 no.4:918-921 O '64. (MIRA 17:11)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR. 2. Chlen-korrespondent AN SSSR (for Shostakovskiy).

SHOSTAKOVSKIY, M.F.; SHERGINA, N.I.; BRODSKAYA, E.I.; YAROSH, O.G.; KOMAROV, N.V.

Vibrational spectra of ethinylsilanes. Dokl. AN SSSR 158 no.5:1143-1145 O '64. (MIRA 17:10)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.
2. Chlen-korrespondent AN SSSR (for Shostakovskiy).

KOMAROV, N.V.; VLASOVA, N.N.

Synthesis of β-silicon-containing vinyl sulfides. Izv. AN SSSR. Ser. khim. no.9:1687-1689 '65. (MIRA 18:9)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

KOMAROV, N.V.; SEMENOVA, N.V.

Synthesis of vinyl esters of organosilicon carboxylic acids.
Izv. AN SSSR.Ser.khim. no.10:1879-1880 '65.
(MIRA 18:10)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

SHERGINA, N.I.; CHIPANINA, N.N.; KOMAROV, N.V.

Determination of basic and acid properties of some oxygen-containing organosilicon compounds by infrared spectroscopy. Izv. AN SSSR. Ser. khim. no.11:2037-2039 '65.

(MIRA 18:11)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

L 5309-66 EWT(m)/EPF(c)/EWP(j) RM

ACC NR: AP5025676 44,55 SOURCE CODE: UR/0286/65/000/018/0025/0025

AUTHORS: Komarov, N. V.; Astaf'yeva, L. N. 44,55

34

B

ORG: none

TITLE: A method for obtaining silicon-bearing β-chloracroleins. 1 44,55 Class 12, No. 174623 15

SOURCE: Byulleten' izobreteniy i tovarnykh znakov, no. 18, 1965, 25

TOPIC TAGS: silicon, beta chloracrolein, siliconacetilene aldehyde, hydrogen chloride, acetic acid

ABSTRACT: This Author Certificate presents a method for obtaining silicon-containing β-chloracroleins. In this method siliconacetilene aldehydes are reacted with hydrogen chloride in acetic acid.

SUB CODE: OC, GC SUBM DATE: 10Aug64/ ORIG REF: 000/ OTH REF: 000

Card 1/1

09010609

SHOSTAKOVSKIY, M.F.; SHERGINA, N.I.; KOMAROV, N.V.

Infrared spectra of some diacetylene organosilicon compounds. Zhur. ob. khim. 35 no.9:1650-1654 S '65. (MIRA 18:10)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

KOMAROV, N.V.; VLASOVA, N.N.; MIKHAYLOV, Z.I.

Synthesis of α-silicon-containing vinyl sulfides. Zhur. ob. khim. 35 no.9:1692 S '65. (MIRA 18:10)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

KOMAROV, N.V.; VLASOVA, N.N.; KAGAN, G.I.; GLADKOVA, G.A.

Synthesis and some conversions of primary γ-silicon acetylene mercaptans. Zhur. ob. khim. 35 no.10:1763-1767 O '65.
(MIRA 18:10)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

SHOSTAKOVSKIY, M.F.; SHERGINA, N.I.; GOLOVANOVA, N.I.; KOMAROV, N.V.;
BRODSKAYA, E.I.; MISYUNAS, V.K.

Vibrational spectra of some organotin acetylenic compounds.
Zhur. ob. khim. 35 no.10:1768-1770 O '65. (MIRA 18:10)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR.

[illegible](m)/EPF(c)/EWP(j)/EWP(t)/EWP(b) Pc-4/Pr-4 IJP(c) JD/RM

[illegible]5005574 [illegible]035/0436

24

[illegible]ostakovskiy, M. F.; Komarov, N. V.; Yarosh, O. [illegible] 22

[illegible]arative method for silicon [illegible]

B

[illegible]rikladnoy khimii, v. [illegible]

[illegible]licon acetylide, ethynylsilane, [illegible]

[illegible] A simple and convenient preparative method employing readily available starting materials has been developed for ethynylsilanes. A trialkylchlorosilare is treated with H_2SO_4 to form the bis(trialkylsilyl) sulface which, in turn, is reacted with monosodium [illegible] inert solvent with heating to form the ethynylsilane [illegible] yield. Orig. art. has: 6 formulas. [SM]

[illegible]: none

SUBMITTED: 12Jun63 ENCL: 00 SUB CODE: GC

NO REF SOV: 005 OTHER: 004 ATD PRESS: 3191

T(m)/EPF(c)/EWP(j) Pc-4/Pr-4 RM
AP5005553 S/0079/65/035/002/0335/0338

akovskiy, M. F.; Komarov, N. V.; Maroshin, Yu. V.

teraction of polyorganosiloxanes with Iotsich's reagent

al obshchey khimii, v. 35, no. 2, 1965, 335-338

TOPIC TAGS: polyorganosiloxane, silicoorganic compound, Iotsich reagent, acetylenic nt, magnesium bromovinylacetylene, dialkylsilanone, acetylenic silanol

The reaction of polorganosiloxanes with acetylenic Grignard compounds (Iotsich's reagent) was studied experimentally studied in order to investigate the served effects of structure on reactivity and establish a possible reaction mechaby the reaction:

$$4CH_2{=}CHC{\equiv}CMgBr + HO[(CH_3)_2SiO]_4H \rightarrow$$

$$\rightarrow 4(CH_3)_2(CH_2{=}CHC{\equiv}C)SiOMgBr \xrightarrow[-H_2O]{HCl}$$

$$\rightarrow 2(CH_3)_2(CH_2{=}CHC{\equiv}C)SiOSi(C{\equiv}CCH{=}CH_2)(CH_3)_2$$

polymethylethylsiloxane to give methylethylvinylethynylsilanol,
ethyl, diethyl- and diisopropylvinylacetylenic silanols were similar-
Pentamethylphenylethynylsiloxane was prepared by reacting polydimethy-
trimethylchlorosilane and an organometallic compound obtained from
moethane and phenylacetylene; (I) was reacted with acetone and tri-
lane to give 1,1-dimethylpenten-4-yne-2-hydroxytrimethylsilane, and
penten-4-yne-2- and 1-methyl-1-ethylpenten-4-yne-2-hydroxymethylethyl-
ed by similar reactions. The results suggest that the reactions

1,1-dimethylpenten-4-yne-2- and 1-methyl-1-ethylpenten-4-yne-2- [illegible]
silane were produced by similar reactions. The results suggest that the reactions
presence of a terminal hydroxyl in the reacting siloxanes, as indica-
us studies, acetylenic magnesiumbromosilanolate being formed as an
intermediate in the synthesis of acetylenic silanols or of symmetric or asymmetric
iloxanes. The analogous formation of magnesiumbromoalcoholates under
itions suggested the presence of "dialkylsilanones" of the formula
he existence of multiple silicon-oxygen bonds in such intermediates is
roposed. Orig. art. has: 11 formulas.

None

8Aug63 ENCL: 00 SUB CODE: OC

007 OTHER: 000

L 35561-65 EPF(c)/EWP(j)/EWA(c)/EWT(m) Pc-4/Tr-4 RM

[illegible] AP5008144 [illegible]/65/000/005/0022/0022

[illegible]stakovskiy, M. F.; Komarov, N. V.; [illegible] B

[illegible] for obtaining silicoacetylen[illegible] [illegible] No. 168622 15

[illegible] izobreteniy i tovarnykh [illegible]

[illegible] magnesium compound, silicoacetylene [illegible] ketone, organic [illegible] tetrahydrofuran

This Author Certificate presents [illegible] silicoacetylene [illegible] broaden the assortment of raw mater[illegible] [illegible]ylethinyl magnesium [illegible] interacted with hydroxyl-bearing [illegible] while being [illegible] medium of an organic solvent [illegible]

[illegible] Irkutskiy institut organicheskoy [illegible] AN SSSR (Irkustk Institute of Organic Chemistry, SO AN SSSR)

[illegible]: 28Jan64 ENCL: 00 SUB CODE: OC

NO REF SOV: 000 OTHER: 000

Card 1/1

L 51684-65 EWT(m)/EPF(c)/EWP(j)/[illegible] Pc-4/Pr-4 RM

ACCESSION NR: AP5010165 UR/0020/65/161/002/0370/0372

[illegible] Shostakovskiy, M. F. (Corresponding member AN SSSR); Komarov, N. V.; [illegible] Sklyanova, A. M.

[illegible] between dialkyl stannic oxide and Iotsich reagent

[illegible] Doklady, v. 161, no. 2, 1965, [illegible]

[illegible] compound, organo metallic compound, [illegible]

The authors examined the reaction between [illegible] xides and [illegible] CMgBr), and they compared the [illegible] with similar [illegible] tones and polydiorganosiloxanes. Dialkyl [illegible] and many [illegible] of stannic chloride are considered to be [illegible] tanes. [illegible] organosiloxanes they should be designated [illegible] and $HO(R_2SnO)_nH$. It might be expected that acetylene stannane alcohols would form from the reaction between dialkyl stannic oxides and Iotsich reagent, but the reaction does not follow the course followed in reactions between C and Si [illegible] reaction of ketones and polydiorganosiloxanes with [illegible] reagent [illegible] by preservation of the C-O and Si-O bonds, whereas the reaction [illegible] stannic oxide with Iotsich reagent leads to destruction of the SnO

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

AP5010165 UR/0020/65/161/002/0370/0372

AUTHORS: Shostakovskiy, M. F. (Corresponding member AN SSSR); Komarov, N. V.; Misyunas, V. K.; Sklyanova, A. M.

24
25
1

Reaction between dialkyl stannic oxide and Iotsich reagent

SSSR. Doklady, v. 161, no. 2, 1965, 370-372

tin compound, organo metallic compound, [illegible]

The authors examined the reaction between dialkyl stannic oxides and [illegible] (RMgBr), and they compared the course of this reaction with similar [illegible] of ketones and polydiorganosiloxanes. Dialkyl stannic oxides and many other derivatives of stannic chloride are considered to be polymeric substances. [illegible] diorganosiloxanes they should be designated by the formulas [illegible] SnO)$_n$H. It might be expected that acetylene stannane alcohols would form from the reaction between dialkyl stannic oxides and Iotsich reagent, but the reaction does not follow the course followed in reactions between C and Si compounds. The reaction of ketones and polydiorganosiloxanes with Iotsich reagent [illegible]sed by preservation of the C-O and Si-O bonds, whereas the reaction [illegible] stannic oxide with Iotsich reagent leads to destruction of the SnO

L 21564-65

ACCESSION NR: AP5010165

[illegible] change of the acetylene group for the [illegible]. The cause of this lies [illegible] and the nature of the bond between the Sn and [illegible] atoms. For the [illegible], an intermediate stage is apparently formed, associated with [illegible] of the dialkyl stannic oxide and with the [illegible] of Mg-Br [illegible]. It is concluded that OHgBr [illegible] changes [illegible] the acetylene radical, [illegible] formation of diacetylene stannanes and [illegible] Mg-Br oxide. The [illegible] down and causes a side splitting reaction with the formation of diacetylene stannanes and brominated dialkyl stannic oxide. These side processes complicate the process. They are avoided and best yields are obtained when using [illegible] Iotsich reagent. Orig. art. has: 11 formulas.

ASSOCIATION: Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya Akademii nauk SSSR (Irkutsk Institute of Organic Chemistry, Siberian Department, Academy of Sciences SSSR)

17Aug64 ENCL: 00 SUB CODE: OC, GC

NO REF SOV: 007 OTHER: 005

Card 2/2

[illegible] m/EPF(c)/EWP(j)/EWA(c) RM

[illegible] AP5018748 UR/0020/65/163/002/0390/0393

56
55
B

[illegible]kovskiy, M.F. (Corresponding member AN SSSR); Komarov, N. V.; Misyunas, V. K.; Sklyanova, A. M.; Burnasheva, T. D.

55

[illegible] Reactions of acetylenes with hexaalkyldistannoxanes

[illegible]R. Doklady, v. 163, no. 2, 1965, [illegible]

[illegible] compound, acetylenic compound

[illegible] It was found that hexaalkyldistannoxanes, in contrast to the corresponding organic and organosilicon analogs, readily react with acetylenic compounds containing an [illegible] to form acetylenic stannanes and stannanols:

$[illegible] + HC \equiv CR' \rightarrow R_3SnC \equiv CR' + R_3Sn[illegible]$

etc.

$R = CH_3, C_2H_5, C_3H_7, C_4H_9$

R' is H, Na, $CH{=}CH_2$, $C{\equiv}CH$, $(CH_3)_3C$, $(CH_3)_3Si$, C_6H_5, $-\underset{|}{C}OH$

$[illegible](OR)CH_2$, $\underset{\underset{O}{\|}}{C}-R$, $CH{=}CHOR$, $CH{=}[illegible]$

Card 1/3

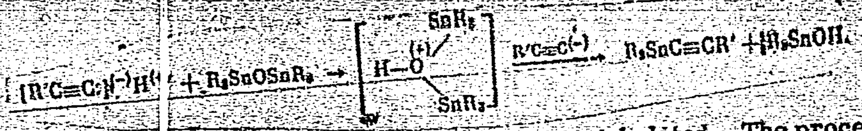
L 62694-65

ACCESSION NR: AP5018748

The reaction is autocatalytic. In addition, the reaction can be caused to take the following course in the presence of excess acetylenic component:

$$R_3SnOSnR_3 + 2R'C\equiv CH \rightarrow 2R_3SnC\equiv CR' + H_2O.$$

The associated side reactions are described. The mechanism of the reaction studied involves an electrophilic proton attack of the oxygen atom and interaction with the acetylenic anion:



The physicochemical constants of the synthesized compounds are tabulated. The procedures followed in the preparation of trimethylethynylstannane, bis (tri-p-propylstannyl)acetylene, triethylstannyldiacetylene, and triethylstannylethynylvinyldiethylamine, and in the reaction of hexaethyldistannoxane with triethylethynylstannane and of the latter with triethylstannanol are described. Orig. art. has: 1 table and 10 formulas.

ACCESSION NR: AP5018748

2

ASSOCIATION: Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya Akademii
tsk Institute of Organic Chemistry, Siberian Branch, Academy of

Jan65 ENCL: 00 SUB CODE: OC

OTHER: 000

L 7896-66 EWT(m)/EPF(c)/EWP(j)/T/EWP(t)/EWP(b)/EWA(c) IJP(c)/RPL

ACC NR: AP5024968 JD/WW/RM SOURCE CODE: UR/0286/65/000/016/0032/0032

AUTHORS: Komarov, N. V.; Shostakovskiy, M. F.; Guseva, I. S.; Misyunas, V. K.

ORG: none

TITLE: Method for obtaining monosubstituted tin acetylenes. Class 12, No. 173758

SOURCE: Byulleten' izobreteniy i tovarnykh znakov, no. 16, 1965, 32

TOPIC TAGS: acetylene, tin compound, organotin compound, organic oxide

ABSTRACT: This Author Certificate presents a method for obtaining monosubstituted tin acetylenes. Organic bisstannic oxides are reacted with acetylene under pressure to 10-11.5 atm at room temperature.

SUB CODE: GC, OC/ SUBM DATE: 25Mar63

nw

Card 1/1 UDC: 547.314.2'13'181.1.07

L 6389-66 EWT(m)/EPF(c)/EWP(j) RM

ACC NR: AP5026741 SOURCE CODE: UR/0286/65/000/017/0016/0016

44,55

INVENTOR: Komarov, N. V.; Yarosh, O. G. 44,5

40
53

ORG: none

44,55

TITLE: A method for producing ethynyl silanes. Class 12, No. 174186

SOURCE: Byulleten' izobreteniy i tovarnykh znakov, no. 17, 1965, 16

TOPIC TAGS: silane, acetylene, sodium, chlorinated organic compound

ABSTRACT: This Author's Certificate introduces a method for producing ethynyl silanes by interacting sodioacetylene with chlorosilanes. The product yield is increased by conducting the process in nitrobenzene.

UDC: 547.419.5.07

SUB CODE: GC,OC/ SUBM DATE: 10Aug64/ ORIG REF: 000/ OTH REF: 000

GC

Card 1/1

SHOSTAKOVSKIY, M.F.; KOMAROV, N.V.; YAROSH, O.G.

Synthesis of trialkylethynylsilanes and silicon acetylene alcohols. Izv. AN SSSR. Ser.khim. no.1:101-104 '66. (MIRA 19:1)

1. Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya AN SSSR. Submitted August 5, 1963.

L 21424-66 EWT(m)/EWP(j)/T/ETC(m)-6 WW/RM

ACC NR: AP6010115 (A) SOURCE CODE: UR/0190/66/008/003/0499/0502 40 B

AUTHOR: Okladnikova, Z. A.; Komarov, N. V.; Semenova, Ye. F.; Serebrennikova, E. V.; Semenova, N. V.; Langvagen, G. G.

ORG: Irkutsk Institute of Organic Chemistry (Irkutskiy institut organicheskoy khimii)

TITLE: Copolymerization of vinyl 3-trimethylsilylpropionate with vinylic monomers

SOURCE: Vysokomolekulyarnyye soyedineniya, v. 8, no. 3, 1966, 499-502

TOPIC TAGS: copolymerization, copolymer, silicon polymer

ABSTRACT: The authors investigated the ability of vinyl 3-trimethylsilylpropionate to copolymerize with vinyl acetate, methyl acrylate, methyl methacrylate, acrylonitrile, and styrene in the presence of azoisobutyronitrile. It was found that vinyl 3-trimethylsilylpropionate can copolymerize with all the above monomers, with the exception of styrene. When the content of vinyl 3-trimethylsilylpropionate in the starting mixture is increased, the yields and molecular weights of the copolymers are decreased. It was shown that, unlike the homopolymers, the copolymers are more easily soluble in organic solvents and have lower melting points The relative [illegible] stability of the copolymerization products with vinyl acetate and methyl [illegible]ate is higher than that of poly(vinyl acetate) and poly(methyl methacrylate) Orig. art. has: 1 table. [VS]

SUB CODE: 11/ SUBM DATE: 07Apr65/ ORIG REF: 002/ OTH REF: 002/ ATD PRESS: 4221

Card 1/1 UDC: 66.095.26+678.13+678.745

UDC: 547.362'345.07

Card 1/1

L 33155-66 EWT(m)/EWP(j) RM

ACC NR: AR6016177 SOURCE CODE: UR/0058/65/000/011/D014/D014

40
B

AUTHOR: Shigorin, D. N.; Gastilovich, Ye. A.; Komarov, N. V.

TITLE: Investigation of compounds of the group $(CH_3)_3\text{-X-C}\equiv\text{CH}$, where X = C, Si, Sn, and Pb in the region of valence oscillations of the groups C-C and C-H

SOURCE: Ref. zh. Fizika, Abs. 11D97

REF SOURCE: Tr. Komis. po spektroskopii. AN SSSR., t. 3, vyp. 1, 1964, 673-678

TOPIC TAGS: absorption band, ir spectrum, complex molecule, molecular physics, molecular interaction

ABSTRACT: The frequencies of the valence oscillation groups $\text{C}\equiv\text{C}$ and $\equiv\text{C-H}$ in compounds $(CH_3)_3\text{-X-C}\equiv\text{H}$ were calculated. The calculated frequencies are compared with the measured frequencies in ir spectra of the compounds $(CH_3)_3\text{-C-C}\equiv\text{CH}$ (I), $(CH_3)_3\text{-Si-C}\equiv\text{CH}$ (II), and $(C_2H_5)_3\text{-SnC}\equiv\text{CH}$ (III). It is concluded that in compounds with Si, Ge, Sn, and Pb there should be observed an intramolecular interaction with participation of the π-electrons of the $\text{C}\equiv\text{C}$ bond, using the d-orbit of the X atom. The presence of such an interaction is confirmed experimentally by the fact that an increase is observed in the intensity of the absorption band of the group $\text{C}\equiv\text{C}$ in II and in III compared with I, and that compounds II and III form stronger complexes with an electro-donor solvent: $(CH_3)_3\text{-X-C}\equiv\text{CH----Y-R}$. [Translation of abstract]

SUB CODE: 07, 20

LS

Card 1/1

L 33266-66 EWP(j)/EWT(m) RM

ACC NR: AR6016190 SOURCE CODE: UR/0058/65/000/011/D024/D024

78
B

AUTHOR: Shostakovskiy, M. F.; Shergina, N. I.; Kagan, G. I.; Komarov, N. V.

TITLE: Investigation of the vibrational spectra of certain carbonyl-containing silicoacetylene compounds

SOURCE: Ref. zh. Fizika, Abs. 11D186

REF SOURCE: Tr. Komis. po spektroskopii. AN SSSR, t. 3, vyp. 1, 1964, 92-98

TOPIC TAGS: silicon compound, acetylene compound, ir spectrum, vibration spectrum, chemical bonding

ABSTRACT: The authors investigated the ir spectra of 16 silicoacetylene compounds which were synthesized for the first time. The frequencies of the vibrations of the fundamental groups are classified. It is shown that the frequency of the oscillations of the acetylene bond, which contains the silicon atom in the α position, changes with the character of the radical R. On the basis of the values of the vibrational frequencies for the bonds $\equiv\mathrm{SiCC}\equiv\mathrm{C}-$ and $-\mathrm{C}\equiv\mathrm{C}-$ it is noted that these bonds do not interact. [Translation of abstract]

SUB CODE: 20, 07

Card 1/1

L 36921-66 EWT(m)/EWP(j) RM

ACC NR: AP6008504 SOURCE CODE: UR/0062/66/000/001/0101/0104 18

B

AUTHOR: Shostakovskiy, M. F.; Komarov, N. V.; Yarosh, O. G.

ORG: Irkutsk Institute of Organic Chemistry, Siberian Department, AN SSSR (Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya Akademii nauk SSSR)

TITLE: Synthesis of trialkylethynylsilanes and silicoacetylene alcohols

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 1, 1966, 101-104

TOPIC TAGS: chemical synthesis, silane, alcohol, ACETYLENE, SILICON COMPOUND

ABSTRACT: In this investigation the authors attempt to find a simpler and more convenient method of synthesizing monosubstituted silicoacetylenes. The reaction of sodium acetylene with bis(trialkylsilyl) sulfates is investigated for the first time. The investigation showed that the reaction occurs normally and leads to the formation of trialkylethynylsilanes with a yield of 60–75%. Higher yields of monosubstituted silicoacetylenes are obtained with the use of bis(trialkylsilyl) sulfates prepared from 100% sulfuric acid. Thus, on the basis of the interaction of trialkylchlorosilanes with sulfuric acid and the subsequent reaction of the organosilicon sulfates that formed with sodium acetylene the authors found a rather simple and readily accessible method of obtaining trialkylethynylsilanes.

Card 1/2 UDC: 542.91+547.362+546.287

L 45912-66 EWT(m)/EWP(j) IJP(c) RM

ACC NR: AP6026427 (A) SOURCE CODE: UR/0079/66/036/005/0904/0907

AUTHOR: Shostakovskiy, M. F.; Komarov, N. V.; Vlasova, N. N.; Rinkus, G. A. 34 B

ORG: Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences, SSSR (Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya Akademii nauk SSSR)

TITLE: Organosilicon vinyl sulfoxides and vinyl sulfones

SOURCE: Zhurnal obshchey khimii, v. 36, no. 5, 1966, 904-907

TOPIC TAGS: organosilicon compound, organic sulfur compound, sulfone, vinyl compound

ABSTRACT: The oxidation of silicon-containing vinyl sulfides of the general structure $R_3Si(CH_2)_nSCH{=}CH_2$ (where n=1,2,3) was carried out under the following conditions: (a) 70% H_2O_2 with cooling to (-10°)-(5°); (b) 30% H_2O_2 in the presence of pyridine with heating to 60°; (c) 70% H_2O_2 in the presence of SeO_2. It was found that the tendency of organosilicon vinyl sulfides to oxidize depends on the relative positions of the sulfur and silicon atoms. The study determined the methods of synthesis of β- and γ-silicon-containing vinyl sulfoxides and vinyl sulfones - heretofore unknown organosilicon sulfur compounds whose composition includes silicon, an unsaturated bond, and polar SO and SO_2 groups. It was noted that the accessibility of the free electron pairs of sulfur in silicon-containing thiovinyl ethers is affected by the trialkylsilyl radical. Thus, as the latter comes closer to the thiovinyl group in the series

UDC: 547.245+547.269

Card 1/2

L 45896-66 EWT(m)/EWP(j) WW/RM

ACC NR: AP6026428 (A) SOURCE CODE: UR/0079/66/036/005/0907/0909

38
29
B

AUTHOR: Komarov, N. V.; Yarosh, O. G.; Astaf'yeva, L. N.

ORG: Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences, SSSR (Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya Akademii nauk SSSR)

TITLE: Synthesis and some conversions of α-silicoacetylene aldehydes

SOURCE: Zhurnal obshchey khimii, v. 36, no. 5, 1966, 907-909

TOPIC TAGS: aldehyde, organosilicon compound, organomagnesium compound

ABSTRACT: A study of the reaction of magnesium derivatives of trialkylethynylsilanes with dimethylformamide showed that trialkylsilylethynylmagnesium bromides readily react with this amide to form previously unknown 1-silicoacetylene aldehydes (in 70% yield):

$$R_3SiC \equiv C\text{-}MgBr + (CH_3)_2NCHO \rightarrow R_3SiC \equiv C\text{-}CHO \; (R = CH_3, C_2H_5, \text{etc.}).$$

The structure of the aldehydes was confirmed by ultimate analysis, physicochemical studies, and some chemical conversions. Thus, the reaction of 2,4-dinitrophenylhydrazine and 3,5-dinitrobenzoylhydrazide produced the corresponding hydrazones. The reaction of α-silicoacetylene aldehydes with the organomagnesium compounds produced

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AUTHOR: Komarov, N. V.; Yarosh, O. G.

ORG: Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences, SSSR (Irkutskiy institut organicheskoy khimii Sibirskogo otdeleniya Akademii nauk SSSR)

TITLE: Ethynylsilanes and some of their conversions

SOURCE: Zhurnal obshchey khimii, v. 37, no. 1, 1967, 264-267

TOPIC TAGS: acetylene compound, silane, organosilicon compound

ABSTRACT: The reactions of trialkylsilylbromomagnesylacetylenes with acid chlorides and anhydrides, ethyl formate, and lead, tin, germanium and silicon chlorides were studied. The reaction with acetic anhydride led to the synthesis of silicoacetylenic ketones:

$$R_3SiC\equiv CMgBr + (CH_3CO)_2O \longrightarrow R_3SiC\equiv C-COCH_3$$

$$R = CH_3, C_2H_5$$

In the reaction with acetyl chloride, tertiary alcohols are formed:

$$R_3SiC\equiv CMgBr + CH_3COCl \longrightarrow (R_3SiC\equiv C)_2C(OH)CH_3$$

With ethyl formate, silicoacetylenic alcohols are also formed:

Card 1/3 UDC: 547.245+547.314.2'13

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Compound	Formula	Yield, %	BP (p in mm)	d_4^{20}	n_D^{20}	MR_D	
						Found	calculated
$(CH_3)_3SiC\equiv CH$	$C_5H_{10}Si$	65.5	52° (735)	0.7055	1.3892	32.92	32.81
$C_2H_5(CH_3)_2SiC\equiv CH$	$C_6H_{12}Si$	61.0	83 (725)	0.7440	1.4084	—	—
$CH_3(C_2H_5)SiH(C\equiv CH)$	$C_5H_{10}Si$	64.5	68 (730)	0.7361	1.4115	33.17	33.03
$(C_2H_5)_2SiH(C\equiv CH)$	$C_6H_{12}Si$	66.7	09 (730)	0.7530	1.4205	37.76	37.66
$CH_3SiH(C\equiv CH)_2$	C_5H_6Si	44.8	67.8 (729)	0.7709	1.4290	31.13	30.89
$CH_3(CH_2{=}CH)Si(C\equiv CH)_2$	C_7H_8Si	49.0	48 (50)	0.8212	1.4513	39.44	30.42
$CH_3Si(C\equiv CH)_3$	C_7H_6Si	32.4	53 (60)	0.8380	1.4522	38.07	37.65
$CH_2{=}CHSi(C\equiv CH)_3$	C_8H_6Si	34.1	61—62 (35)	0.8844	1.4734	41.34	41.91
$Si(C\equiv CH)_4$	C_8H_4Si	12.8	MP 101°	—	—	—	—
$C_2H_5(CH_3)_2SiC\equiv C{-}COCH_3$	$C_8H_{14}OSi$	63.6	70—71 (15)	0.8658	1.4488	47.78	47.19
$[(CH_3)_3SiC\equiv C]_2CHOH$	$C_{10}H_{20}OSi_2$	61.8	120—121 (10)	0.8834	1.4690	70.75	70.65
$[(CH_3)_3SiC\equiv C]_4Ge$	$C_{20}H_{36}GeSi_4$	95.1	MP 160°	—	—	—	—
$[(CH_3)_3SiC\equiv C]_4Sn$	$C_{20}H_{36}Si_4Sn$	34.8	MP 140° (dec.)	—	—	—	—
$[(CH_3)_3SiC\equiv C]_4Pb$	$C_{20}H_{36}PbSi_4$	47.2	MP 108°	—	—	—	—

Card 2/3

$$R_3SiC\equiv CMgBr + HCOOC_2H_5 \longrightarrow (R_3SiC\equiv C)_2CHOH$$
$$R = CH_3,\ C_2H_5$$

The reactions with chlorides of group IV elements were:

$$4R_3SiC\equiv CMgBr + ECl_4 \longrightarrow (R_3SiC\equiv C)_4E$$
$$4R_3SiC\equiv CMgBr + 2PbCl_2 \longrightarrow (R_3SiC\equiv C)_4Pb + Pb$$
$$R = CH_3;\ E = Si,\ Ge,\ Sn.$$

The synthesized compounds and their constants are shown in Table 1. Orig. art. has: 1 table.

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ZOLOTYY, S.G.

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KOMAROV, N.V.

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