62-2-12/28

AUTHORS: Shostakovskiy, M. F., Chekulayeva, I. A.

TITLE: Synthesis and Conversions of the Vinyl Ethers of Ethanol-Amines (Sintez i prevrashcheniya vinilovykh efirov etanolaminov). Report 9: Quaternary Ammonium Salts of the Vinyl Ethers of Ethanol Amines (Soobshcheniye 9. Chetverichnyye ammoniyevyye soli vinilovykh efirov etanolaminov).

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 2, pp. 204-209 (USSR).

ABSTRACT: The investigation of the properties of the interaction products of the above-mentioned vinyl ethers with alkyl halides is a natural continuation of the investigation of the reactivity of the double bond of the vinyl ethers of ethanol amines. This bond depends on the nature of the amino group and increases with the replacement of free hydrogens by alkyl- and phenyl-radicals. The influence of the amino group can be excluded by means of addition compound of the alkyl halides to the nitrogen of the vinyl ethers of ethanol amines. In the investigation the authors used the vinyl ether of β-(diethylamino)-ethanol, the vinyl ether of β-(diphenylamino)-ethanol and the trivinyl ether of triethanol amine. Quaternary

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62-2-12/28

Synthesis and Conversions of the Vinyl Ethers of Ethanol-Amines. Report 9: Quaternary Ammonium Salts of the Vinyl Ethers of Ethanol Amines.

ammonium salts of β-(diethylamino)-ethanol, of the vinyl ether of β-(diethylamino)-ethanol and some derivatives of it (with CH_3, C_2HJ and C_2H_5Br) were obtained. The authors investigated some conversions of the quaternary ammonium salts of the vinyl ether of β-(diethylamino)-ethanol (hydrolysis, polymerization, interaction with alcohols and organic acids). The authors examined the interaction of the trivinyl ether of triethanol-amine and the vinyl ether of β-(diphenylamino)-ethanol with methyl iodide and ethyl bromide. There are 1 table and 5 references, 5 of which are Slavic.

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

SUBMITTED: September 28, 1956

AVAILABLE: Library of Congress

Card 2/2

1. **Vinyl ethers of ethanol-amines-Synthesis** 2. **Quaternary ammonium salts**

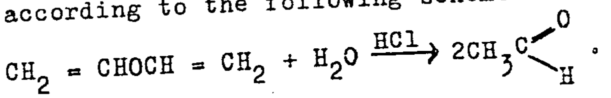
62-58-3-14/30

AUTHORS: Shostakovskiy, M. F., Dubrova, Ye. V.

TITLE: Synthesis and Conversions of Divinyl Ether (Sintez i prevrashcheniya divinilovogo efira)

PERIODICAL: Izvestiya Akademii Nauk SSSR,Otdeleniye Khimicheskikh Nauk, 1958, Nr 3, pp. 339-343 (USSR)

ABSTRACT: The above-mentioned ether has hitherto only been used in surgical practice. Only after a thorough investigation of the divinyl ethers it is possible to evaluate the possibility of their use also in other domains. The authors occupied themselves with the investigation of the properties of this ether and found: According to its structure ($CH_2 = CHOCH = CH_2$) it belongs to the simplest ethers. Under the influence of ferric chloride and stannic chloride it cannot be polymerized. In this paper it is shown that divinyl ether quantitatively splits according to the following scheme:



$CH_2 = CHOCH = CH_2 + H_2O \xrightarrow{HCl} 2CH_3C\begin{smallmatrix}O\\H\end{smallmatrix}$. Then the authors describe the properties of divinyl ether. The addition of

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Synthesis and Conversions of Divinyl Ether

62-58-3-14/30

hydrogen chloride was performed according to a method already described earlier (Ref. 14). The reaction takes place in steps:

1. $CH_2 = CHOCH = CH_2 + HCl \longrightarrow CH_2 = CHOCHCICH_3$

2. $CH_2 = CHOCHCICH_3 + HCl \longrightarrow CH_3CHClOCHClCH_3$. In the case of addition of one hydrogen chloride molecule the authors obtained vinyl-α-chlorethyl ether. In the case of addition of 2 molecules of hydrogen chloride they obtained ,however, α,α'-dichlorethyl-ether. The chlorination was performed according to the method worked out for the synthesis of the α,β-dichlorethylalkyl-ethers (Ref. 15).

The authors synthesized and described: vinyl-α-ethyl-ether, α,α'-dichlorodiethyl-α,α',β,β'-tetrachlorodiethyl- and α,α',β,β'-tetrabromodiethyl-ether. There are 16 references, 3 of which are Soviet.

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

SUBMITTED: November 9, 1956

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SHOSTAKOVSKIY, M.F.

62-58-4-28/32

AUTHORS: Shostakovskiy, M. F., Khomenko, A. Kh.

TITLE: Letters to the Editor (Pis'ma redaktoru)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 4, p. 519 (USSR)

ABSTRACT: The formation of diacetylene on the action of alcoholic alkali on 1,4-dichlorobutyne-2 was found already long ago. The mechanism of this reaction remained, however, unclear. The authors found that in the interaction of the methanol solution of caustic potash with 1,4-dichlorobutyne-2 the latter (reacting in its isomeric form of 2,3-dichlorobutadiene-1,3) forms a number of products according to reaction conditions. The following compounds were synthetized: 1-methoxy-2,3-dichlorobutene-2, boiling point: 50° C (5 mm), d_4^{20} 1,2090; n_D^{20} 1,4910; 2-chlorobutene-1-in-3, boiling point: 63-65°C (760 mm); d_4^{20} 1,030; n_D^{20} 1,4720; 2-chloro-4-methoxy-

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62-58-4-28/32

Letters to the Editor

butadiene-1, boiling point: 50°C(8 mm); d_4^{20} 1,2179; n_D^{20} 1,4680; 2-chloro-4,4-dimethoxybutene-1,boiling point: 66°C(22 mm); d_4^{20} 1,0262; n_D^{20} 1,4535; diacetylene, melting point: -36°C;boiling point: 10°C;4-methoxybutene-3-in-1, boiling point: 50°C(50 mm); d_4^{20} 1,9113; n_D^{20} 1,4770;boiling point 56°C (50 mm); d_4^{20} 0,8987; n_D^{20} 1,4820 and 1,1-dimethoxy-2-butin, boiling point:52-53°C(12 mm); d_4^{20} 0,9577; n_D^{20} 1,4359 (see formulae I to VIII).

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Letters to the Editor 62-58-4-28/32

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

SUBMITTED: January 17, 1958

AVAILABLE: Library of Congress

1. Cyclic compounds--Synthesis

Card 3/3

AUTHORS: Shostakovskiy, M. F., Chekulayeva, I. A. SOV/62-58-6-33/37
Kondrat'yeva, L. V.

TITLE: Letter to the Editor (Pis'ma redaktoru)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 6, pp. 794 - 794 (USSR)

ABSTRACT: Recently increased interest has been displayed by research workers in the chemistry of diacetylene. In the course of the present report the authors describe some of the peculiar features of the interaction between diacetylene and some aminoalcohols. It was shown that β-(diethylamino)ethanol enters into reaction with diacetylene (contrary to non-substituted alkyl esters) without a catalyzer. On this occasion 1-(β-diethylamino)ethoxybutene-in-3 (Formula I) with 80-90% yield is formed. Ethinylvinyl ester combines with the 2.molecule of β-(diethylamino)ethanol under more rigorous conditions. This causes the formation of: Di-(β-diethylaminoethoxy)buthadien-1,3 with 55-60% yield:

$$\xrightarrow{(C_2H_5)_2NCH_2CH_2OH} (C_2H_5)_2NCH_2CH_2OCH{=}CH{-}CH{=}CHOCH_2CH_2N(C_2H_5)_2.$$

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Letter to the Editor SOV/62-58-6-33/37

In the case of buthyl alcohol the following acetal was obtained: $CH_3 - C \equiv C - CH(OC_4H_9)\ OCH_2CH_2N(C_2H_5)_2$. The structure of the compounds obtained was ascertained by means of hydrolysis and spectral analysis.

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

SUBMITTED: April 16, 1958

1. Acetylenes--Chemical reactions 2. Amino alcohols--Chemical reactions 3. Spectrographic analysis--Applications 4. Cyclic compounds--Hydrolysis

Card 2/2

SOV/62-58-8-12/22

AUTHORS: Bogdanova, A. V., Shostakovskiy, M. F., Krasil'nikova, G. K.

TITLE: Investigation in the Field of Vinylaryl Ethers (Issledovaniye v oblasti vinilarilovykh efirov) Note 7: Ion- and Radical Polymerization of the Simple Vinyl Ether of Cyclohexanol, β-Decalol and β-Naphthol (Soobshcheniye 7. Ionnaya i radikal'naya polimerizatsii i sopolimerizatsii prostykh vinilovykh efirov tsiklogeksanola, β-dekalola i β-naftola)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 8, pp. 990-995 (USSR)

ABSTRACT: In publications there have hitherto been no notes concerning the polymerization of vinyl-β-naphthyl- and vinyl-β-decalyl ether under the action of the nitryl of azoisobutyric acid. In the previous papers the authors dealt with the polymerization of vinyl-phenyl and vinyl paraternary butyl-phenyl ether (Refs 1-3) as well as with their copolymerization with vinyl ether and vinyl-butyl ether. The present paper deals with the investigation of the conditions required for the polymerization and copolymerization of vinyl-β-naphthyl-, vinyl-β-decalyl-

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SOV/62-58-8-12/22

Investigation in the Field of Vinylaryl Ethers. Note 7: Ion- and Radical Polymerization of the Simple Vinyl Ether of Cyclohexanol, β-Decalol and β-Naphthol

and vinyl-cyclohexyl ether under the action of BF_3, the benzoyl peroxide and the nitrile of the azoisobutyric acid. The conditions were found on which the polymers of vinyl-cyclohexyl, vinyl-β-decalyl-and vinyl-β-naphthyl ether (and their copolymers) with vinyl ethyl, vinyl-butyl and vinyl-phenyl ether may be produced in good yields on the action of the BF_3-

etherate. The majority of these polymers consists of solid products. It could further be found that the polymerization of vinyl-cyclohexyl, vinyl-β-decalyl- and vinyl-β-naphthyl ether on the action of benzoyl and nitrile peroxide of the azoisobutyric acid needs a great amount (up to 6%) of the initiator; more heating and more time. The polymer yield is small. Vinyl-cyclohexyl-, vinyl-β-decalyl- and vinyl-phenyl ether can, under the action of benzoyl peroxide, be included into the copolymerization with methyl ethers of the acrylic and methacrylic acid. On this occasion copolymers of divers structures are formed which contain simple vinyl ethers (up to 44%).

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Investigation in the Field of Vinylaryl Ethers. Note 7: Ion- and Radical Polymerization of the Simple Vinyl Ether of Cyclohexanol, β-Decalol and β-Naphthol SOV/62-58-8-12/22

There are 6 tables and 10 references, 8 of which are Soviet.

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

SUBMITTED: January 9, 1957

Card 3/3

SHOSTAKOVSKIY, M. F.

"Polyvinylpyrrolydone is obtained and how it is used as blood substitute"

report presented at the 10th All-Union Conf. on Highly Molecular Compounds, Biologically Active Polymer Compounds, Moscov, 11-13 June 1958. (Vest. Ak Nauk SSSR, 1958, No. 9, pp. 111-113)

AUTHORS: Prilezhayeva, Ye. N., Shostakovskiy, M. F. SOV/62-58-9-14/26

TITLE: Synthesis of Sulfur-Containing Compounds on the Basis of Vinyl Ether and Acetylene (Sintez serusoderzhashchikh veshchestv na osnove vinilovykh efirov i atsetilena) Communication 16: The Mobility of the β-Alkoxy Groups in Ethylalkyl and Aryl Sulfides (Soobshcheniye 16. O podvizhnosti β-alkoksigrupp v etilalkil- i arilsul'fidakh)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 9, pp 11o4 - 111o (USSR)

ABSTRACT: There are many papers dealing with the hydrolysis reactions of β-chloro- and bromo-ethylalkyl (aryl) sulfides and Yperite (dichlorodiethyl sulfide) as well as the substitution reactions involving their halides. There are no papers, except that of Kretov (Ref 7), which deal with the substitution of alkoxy groups in β-alkoxyalkyl sulfides. As a result of their investigations the authors of this paper were able to determine optimal reaction conditions for the preparation of the products (contrary to Markovnikov's rule) of the reaction between vinylalkyl esters and mercaptans. They were also able to prepare with good yield a series

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Synthesis of Sulfur-Containing Compounds on the Basis of SOV/62-58-9-14/26
Vinyl Ether and Acetylene. Communication 16: The Mobility of the β-Alkoxy
Groups in Ethylalkyl and Aryl Sulfides

of 1-alkoxy-2-alkyl (aryl) mercaptans. It was shown that in 1-alkoxy-2-alkyl(aryl) mercaptans the alkoxy group can easily be replaced by chlorine. A series of 1-chloro-2-alkyl(aryl)mercaptans were synthesized according to the following general reaction:

$$C_4H_9OCH = CH_2 \xrightarrow{RSH} C_4H_9OCH_2CH_2SR \xrightarrow{HCl} ClCH_2CH_2SR.$$

It is assumed that the reaction involving the formation of the ethylenesulfo ion occurs, which would then explain the dependence (found in this work) of the case of exchange of the alkoxy group upon the structure of other parts of the starting (reactant) sulfide. There are 3 tables and 13 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, AS USSR)

SUBMITTED: February 8, 1957

Card 2/2

AUTHORS: Sidel'kovskaya, F. P., Zelenskaya, M. G., SOV/62-58-9-15/26
Shostakovskiy, M. F.

TITLE: **Studies in the Field of** Lactones and Lactams (Issledovaniye v oblasti laktonov i laktamov) Communication 12: Vinyl Ether of N-(β-Oxyethyl)Pyrrolidone (Soobshcheniye 12. Vinilovyy efir N-(β-oksietil)pirrolidona)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 9, pp 1111 - 1118 (USSR)

ABSTRACT: During the last year various nitrogen-containing vinyl compounds with remarkable properties were synthesized. The authors of this paper attempted to prepare the vinyl ether of N-(β-oxyethyl) lactam in order to study its properties and in order to compare the properties of the vinyl ethers of N-substituted β-ethanolamine with those of the vinyl lactams. The vinyl ether of N-(β-oxyethyl) pyrrolidone was synthesized. In addition the authors investigated the reaction between δ -valerolactone and ethanolamine at 200° C. Under the reaction conditions the 6-membered ring apparently opens. Using the example

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Studies in the Field of Lactones and Lactams. SOV/62-58-9-15/26
Communication 12: Vinyl Ether of N-(β-Oxyethyl)Pyrrolidone

of the reaction of the compound with butanol it was shown that the vinyl ether of N-(β-oxyethyl)pyrrolidone combines with alcohols. Di-N-(ethylpyrrolidonyl)acetal and butyl-N-(ethylpyrrolidonyl) acetal were isolated. The thermal decomposition of butyl-N-(ethylpyrrolidonyl) acetal was investigated. It was shown that the vinyl ether of N-(β-oxyethyl)pyrrolidone combines with hydrogen chloride. The product formed is unstable and upon standing is transformed into the chlorohydrate of N-(β-oxyethyl)pyrrolidone. It was found that the vinyl ether of N-(β-oxyethyl)pyrrolidone polymerizes under the influence of the dinitrile of isobutyric acid vapor and hydrogen peroxide. It tends to polymerize thermally, but in the presence of 0,2% benzoyl peroxide (at 60° C) it does not polymerize. There are 2 tables and 9 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, AS USSR)

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SHOSTAKOVSKIY, M.F

5

4E2c(j)

2J (NB)

4E3d

Chemistry of vinyl compounds. M. F. Shostakovskii (N. D. Zelinskii Inst. Org. Chem., Moscow). —*Chemie* (Prague) 10, 273-92(1958).—A review with 76 references referring to the work of the author's lab. Vinylation by means of acetylene is illustrated by examples. The article deals with properties and reactions of following classes of compds.: vinyl alkyl ethers (halogenation, addn. of substances contg. mobile H, addn. of org. acids, addn. of H_2S and mercaptans); vinyl aryl ethers; α-methylvinyl alkyl ethers; vinyl ethers of ethanolamines; vinyl chlorosilanes; vinyl sulfides; vinyl lactams (vinylpyrrolidone, -piperidone, and -caprolactam). I. M. Hais

C7K

AUTHORS: Shostakovskiy, ~~M. F.~~, Prilezhayeva, Ye. N., SOV/62-58-10-14/25
Uvarova, N. I.

TITLE: The Synthesis of Sulfur Compounds on the Basis of Vinyl Ethers and Acetylene(Sintez sernistykh veshchestv na osnove vinilovykh efirov i atsetilena) Communication 17. Vinyl Ether of Monothioethylene Glycol (Soobshcheniye 17. Vinilovyye efiry monotioetilenglikolya)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 10, pp 1245 - 1249 (USSR)

ABSTRACT: In earlier papers (Refs 1,2) it was shown that the double bond in the α,β position to the sulfur atom is considerably less active in ion reactions of the compound and in polymerizations, than the same bond under the action of the oxygen atom. In the present paper the authors mention some data on the chemical behaviour of vinyl ether of monothioethylene glycol. Its complete vinyl ether is of interest as it contains in one molecule both types of double bonds. In the vinylation of monoethylene glycol its S-vinyl ether

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The Synthesis of Sulfur Compounds on the Basis of Vinyl Ethers and Acetylene. Communication 17. Vinyl Ether of Monothioethylene Glycol

SOV/62-58-10-14/25

is formed in good yield: 1-vinyl mercapto-2-oxy-ethane, which points to the relatively high reactivity (under the conditions of the mercapto group as compared to that of the hydroxyl group). The obtained 1-vinyl mercapto-2-oxy ethane has the same chemical properties of the not substituted thiovinyl ether. In the reaction with ethyl mercaptane (in contrast to other thiovinyl ethers, Refs 1,6) a mixture of the combination products is formed. Under the action of dinitrile of the azoiso butyric acid a polymer is formed with a three-dimensional structure (by partly linking at the expense of the oxy groups, as this polymer can not be dissolved in any of the solvents under review). The authors showed that the double bonds in 1-mercapto-2-vinyl ethane under the action of oxygen and sulfur are characterized by their easy ion reactions especially the reaction of the hydrolysis in acid medium. There are 1 table and 9 references, 6 of which are Soviet.

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The Synthesis of Sulfur Compounds on the Basis of Vinyl Ethers and Acetylene. Communication 17. Vinyl Ether of Monothioethylene Glycol SOV/62-58-10-14/25

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

SUBMITTED: February 8, 1957

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AUTHORS: Shostakovskiy, M. F., Prilezhayeva, Ye. N., Karavayeva, V. M. SOV/62-58-10-15/25

TITLE: Synthesis of Sulfur Compounds From Vinyl Ethers and Acetylene(Sintez sernistykh veshchestv na osnove vinilovykh efirov i atsetilena)Communication 18. S-Vinylmercaptobenzothiazole(Soobshcheniye 18. S-vinilmerkaptobenzotiazol)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 10, pp 1250 - 1253 (USSR)

ABSTRACT: The authors were interested in synthesizing vinyl sulfides having nitrogen atoms in the molecule, as well as to study their properties. Mercapto benzothiazole "Captax" which in the crystalline state has the thion form, at higher temperatures, however, and in alkaline medium easily passes over into the thiol form was chosen as initial compound of the synthesis. S-vinyl mercapto benzothiazole was produced by the action of acetylene on captax. Besides, potassium mercapto benzothiazole was separated from the reaction mixture. Potassium mercapto benzothiazole was used as catalyst

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Synthesis of Sulfur Compounds From Vinyl Ethers and Acetylene. Communication 18. S-Vinylmercaptobenzothiazole SOV/62-58-10-15/25

by which fact the yield of the vinylation product could be increased. In the vinylation the corresponding mercaptide occurs as catalyst, with the reaction of acetylene with the mercaptide ion determining the velocity of the process. The other reactions of vinyl mercapto benzothiazole are similar to the reactions of aliphatic thiovinyl ether. Finally the authors discussed the transformations of S-vinyl mercapto benzothiazole, as the reaction of S-vinyl mercapto benzothiazole and sublimate as well as the formation of β-ethyl mercapto-S-ethyl mercapto benzothiazole. There are 3 tables and 9 references, 4 of which are Soviet.

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

SUBMITTED: February 22, 1957

Card 2/2

SHIKHIYEV, I.A.; SHOSTAKOVSKIY, M.F.; KAYUTENKO, L.A.

Investigations in the synthesis and conversion of unsaturated silicon organic compounds. Dokl. AN Azerb.SSR 14 no.9:687-689 '58. (MIRA 11:10)

1. Institut organicheskoy khimii AN SSSR im. N.D.Zelinskogo i Institut nefti AN AzerSSR. Predstavleno akademikom AN AzerSSR Yu.G.Mamedaliyevym.

(Silicon organic compounds)

SOV/74-27-10-4/4

AUTHORS: Shostakovskiy, M. F., Kochkin, D. A., Vinogradov, V. L. (Moscow)

TITLE: The Unsaturated Silicon Compounds (Nepredel'nyye soyedineniya kremniya)

PERIODICAL: Uspekhi khimii, 1958, Vol 27, Nr 10, pp 1221-1256 (USSR)

ABSTRACT: Early in this paper the authors deal with the importance of such silicon compounds which have alkyl or alkene groups at the silicon atom. In the USSR as well as abroad abundant scientific publications on the unsaturated silicon compounds are available. The first part of this report is devoted to the vinyl compounds of silicon. In section 1 the following methods for the production of vinyl silane are discussed: a) the production of vinyl chlorosilanes from vinyl chloride and silicon by means of direct synthesis; b) the production of vinyl alkyl silanes and halogen vinyl silanes by means of dehydrochlorination of the chloroalkyl silanes; c) organometallic synthesis of the vinyl compounds of silicon; d) the organolithium synthesis; e) vinylation of the silanes by means of acetyls; f) production of organosilicic vinyl ethers. In the second section the physical properties of the vinyl silanes are discussed. Section three deals

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SOV/74-27-10-4/4

The Unsaturated Silicon Compounds

with the chemical properties of the vinyl silanes: a) interaction between the halogen vinyl silanes and alcohols; b) reaction with ethylene chlorohydrin; c) hydrohalogenation; d) hydrolysis and cohydrolysis; e) combination with aldehydes; f) combination with dialkyldithiophosphoric acids; g) combination with thiocyanogen; h) Friedel-Krafts reaction; i) dienesynthesis; k) the combination with chloroform and tetrachlorosilicon; l) interaction with carbon oxide and hydrogen (oxosynthesis). The second part of the paper treats the allyl compounds of silicon. Section 1: diverse methods for the production of allyl silanes: a) direct synthesis of the allyl chlorosilanes; b) organomagnesium synthesis of the allyl compounds of silicon; c) organolithium synthesis of the α- and β-alkenyl compounds of silicon; d) hydrogenation of the allyl chlorosilanes; e) production of halogen alkenyl silanes by combination with butadiene; section 2: the physical properties of the allyl silanes; section 3: the chemical properties of the allyl compounds of silicon: The interaction with hydrogen bromide and hydrogen iodide, with hydrogen chloride, with halides; hydrogenation of the allyl silanes, reaction with sulfuric acid etc. Part 3: Unsaturated organosilicic compounds of the acetylene series: section 1:

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methods for the production of organosilicic compounds of the acetylene series; section 2: physical properties of the organosilicic compounds of the acetylene series. Section 3: chemical properties of the organosilicic compounds of the acetylene series. Part 4 of the paper deals with the polymerization and the copolymerization of unsaturated compounds of silicon. Section 1: polymerization. Section 2: copolymerization. There are 3 tables and 119 references, 70 of which are Soviet.

79-28 3-3/61

AUTHORS: Shostakovskiy, M. F., Kulibekov, M. R.

TITLE: Investigation of the Substitution Reaction of Oxyradicals by the Radicals of Organic Magnesium Compounds (Issledovaniye reaktsii obmena oksi-radikalov na radikaly magniyorganicheskikh soyedineniy). I. Investigation of the Reaction of Mixed Acetals (I. Issledovaniye reaktsionnosposobnosti smeshannykh atsetaley)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 3, pp. 578-584 (USSR)

ABSTRACT: In the present investigation Grignard's reagent is used in order to determine the mobility of oxyradicals in mixed acetals, which problem has not been investigated in publications until now. The characteristic feature of acetals is their high reactivity with simple vinyl ethers (scheme 1). As regards the structure of the mixed acetals it was found by thermal decomposition (scheme 2) as well as by spectroscopic investigation according to the combination method of diffuse light that, e. g. mixed

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79-28-3-3/61

Investigation of the Substitution Reaction of
Oxyradicals by the Radicals of Organic Magnesium Compounds.
I. Investigation of the Reaction of Mixed Acetals

alkylarylacetals can be present in two forms (scheme 3). As mixed acetals are constantly demanding greater theoretical and practical interest the authors set to the task of exactly investigating the mobility of their oxygroups with the Grignard reagent. Three groups of mixed acetals were subjected to this investigation, that is to say: 1. dialkyl-, 2. alkylaryl-, and 3. alkylfataromatic acetals. With the action of magnesium bromobutyl on the same acetal no substitution of the ethoxy- and butoxygroup takes place. In the reaction of magnesium bromobutyl with ethylbenzylacetal and ethylphenylacetal always only the ethylether of hexanol-2 (scheme 5) is formed. The action of magnesium bromophenyl on ethylbutyl-, ethylbenzyl- and ethylphenylacetal in all cases leads to one and the same ether as main product (scheme 6). By their findings the authors come to the conclusion that the mobility or reactivity of oxyradicals of mixed acetals is dependent on their electron structure, which makes easier the splitting of the O Ar group as anion (ref. 5) under the formation of a carbonium ion. (Scheme 7).

There are 8 references, 6 of which are Soviet.

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79-28 -3-3/61

Investigation of the Substitution Reaction of Oxyradicals by the Radicals of Organic Magnesium Compounds

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR i Azerbaydzhanskiy sel'skokhozyaystvennyy institut (Institute for Organic Chemistry AS USSR and Azerbaydzhan Agricultural Institute)

SUBMITTED: February 18, 1957.

Card 3/3

79-28-4-23/60

AUTHORS: Shostakovskiy, M. F., Kulibekov, M. R.

TITLE: Investigation of the Exchange Reaction of Oxide Radicals With Radicals of Organomagnesium Compounds (Issledovaniye reaktsii obmena oksiradikalov na radikaly magniyorganicheskikh soyedineniy) II. Interaction of the Grignard Reagent With Symmetric Acetals (II Vzaimodeystviye reaktiva Grin'yara s simmetrichnymi atsetalyami)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 4, pp. 951-954 (USSR)

ABSTRACT: In the present paper the authors investigated the effect of the Grignard reagent on symmetric acetals of the aliphatic, aliphatic-aromatic and aromatic series. They worked out synthesis conditions for the respective monoethers, also comprising those difficultly accessible. Moreover, they established the specific effect of single radicals of the Grignard reagent, which take part in the exchange reaction with symmetric acetals. On the basis of experimental data it can be stated with respect to the reactivity of symmetric acetals that, contrary to mixed acetals, they show a number of peculiarities, which are connected with the presence of

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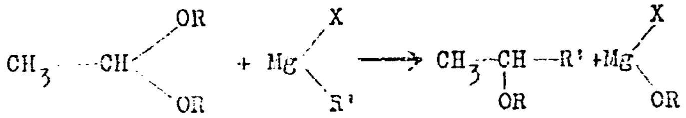
79-28-4-23/60

Investigation of the Exchange Reaction of Oxide Radicals With Radicals of Organomagnesium Compounds. II. Interaction of the Grignard Reagent With Symmetric Acetals

identical oxyradicals. This produces a certain equilibrium of their molecules, at a disturbance of which the exchange reaction proceeds entirely smoothly according to the scheme



R denoting alc. ar or an aliphatic-aromatic radical. Three groups of symmetric acetals were employed in the investigation: dialkyl-, diaryl-, and symmetric, aliphatic-aromatic acetals. It was found that the phenoxy group reacts most easily, whereas the aliphatic-aromatic oxyradicals react considerably more difficultly, the alkoxy groups taking an intermediate position. For the first time were synthesized: The butyl-ether of 2-methylhexanol-5, of the secondary phenylpropyl- and phenylethyl alcohols; the benzilether of the secondary phenylpropyl- and phenylethyl alcohols; the phenylether of the hexanol-2 and dibenzilacetal. There are 1 table and 3 references, 3 of which are Soviet.

Card 2/3

79-28-4-23/60

Investigation of the Exchange Reaction of Oxide Radicals With Radicals of Organomagnesium Compounds. II. Interaction of the Grignard Reagent With Symmetric Acetals

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR i Azerbaydzhanskiy sel'skokhozyaystvennyy institut (Institute for Organic Chemistry, AS USSR, and Azerbaydzhan Institute for Agriculture)

SUBMITTED: March 21, 1957

Card 3/3

79-28-5-28/69

AUTHORS: Shostakovskiy, M. F., Gracheva, Ye. P., Kul'bovskaya, N. K.

TITLE: Investigations in the Field of the Synthesis and Conversions of Substituted Vinylethers (Issledovaniye v oblasti sinteza i prevrashcheniy zameshchennykh vinilovykh efirov) VI. Synthesis of α-Methylvinylarylether and of α-Methylvinylcyclohexylether (VI Sintez α-metilvinilarilovykh i α-metilviniltsiklogeksilovogo efirov)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 5, pp. 1253-1257 (USSR)

ABSTRACT: In face of certain unclear problems of the syntheses of α-methylvinylarylether carried out by Ruhemann, Wragg (Rueman i Vreg) on the one hand (reference 1) and Niederl, Storch (Niderl i Storkh) (reference 2) on the other hand, this paper investigates more detailed the synthesis of α-methylvinylarylether and of α-methylvinylcyclohexylether according to Favorskiy-Shostakovskiy.

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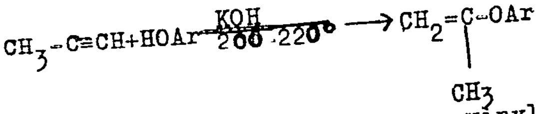
79-28-5-28/69

Investigations in the Field of the Synthesis and Conversions of Substituted Vinylethers. VI. Synthesis of α-Methylvinylarylether and of α-Methylvinylcyclohexylether



$$CH_3-C\equiv CH+HOAr \xrightarrow[200-220^\circ]{KOH} CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-OAr$$

The use of methylacetylene as vinylation medium yields less than that of acetylene in the vinylation of phenols (references 3, 4). This method is, however, the best accessible in the synthesis of the above mentioned ethers. The best results (yield and better avoidance of resinification) was obtained at a ratio of 1 molecule of phenol and 1 molecule of caustic potash (table 1). It was of interest to investigate the part of the allene (propadiene) in this vinylation reaction with the initial methylacetylene. The allene is contained in the initial product (reference 5) and is the result of an isomerization $CH_3C\equiv CH \rightleftarrows C=CH_2$. According to Favorskiy (reference 6) the isomerization of the acetylene-and allene hydrocarbons

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79-28-5-28/69

Investigations in the Field of the Synthesis and Conversions of Substituted Vinylethers. VI. Synthesis of α-Methylvinylarylether and of α-Methylvinylcyclohexylether

belong to those being reversible. In the present case the equilibrium is displaced toward methylacetylene (at 200° - 10% allene against 90% methylacetylene!). In order to explain the role of allene under the given conditions it was heated to 200°C in the autoclave with 50% caustic potash solution, in which case the allene converted into the methylacetylene which was separated in form of acetylenide. From table 2 can be concluded that in the vinylation of the phenols with allene and methylacetylene the allene can not be considered as vinylation medium, but that it is isomerized to methylacetylene which then supplies the actual vinylation medium. The structure of the synthetized α-methylsubstituted ether was proved by hydrolysis. There are 3 tables and 16 references, 12 of which are Soviet.

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79-28-5-28/69

Investigations in the Field of the Synthesis and Conversions of Substituted Vinylethers. VI. Synthesis of α-Methylvinylarylether and of α-Methylvinylcyclohexylether

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute for Organic Chemistry, AS USSR)

SUBMITTED: April 24, 1957

Card 4/4

SOV/79-28-6-22/63

AUTHORS: Shostakovskiy, M. F., Kulibekov, M. R., Shikhiyev, I. A.

TITLE: Investigation of the Substitution Reaction of Oxy Radicals by Radicals of Organomagnesium Compounds (Issledovaniye reaktsii obmena oksiradikalov na radikaly magniyorganicheskikh soyedineniy) III. Conversion of Organomagnesium Compounds With Mixed Organosilicon Acetals (III. Vzaimodeystviye magniyorganicheskikh soyedineniy so smeshannymi kremniyorganicheskimi atsetalyami)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1539-1542 (USSR)

ABSTRACT: In earlier papers (Ref 1) the authors investigated the effect of the Grignard reagents with respect to the mixed and asymmetric organic acetals, and they found that in the mixed acetals the oxy radicals are in the first place substituted by the Grignard radical under the formation of ethers. With respect to the substitution of the oxy radicals in the symmetric acetals the following sequence shows up: OAr > OAlk > > $OCH_2C_6H_5$. This rule was explained by the presence of a

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SOV/ 79-28-6-22/63

Investigation of the Substitution Reaction of Oxy Radicals by Radicals of Organomagnesium Compounds. III. Conversion of Organomagnesium Compounds With Mixed Organosilicon Acetals

certain bond position, by which one of the oxy radicals becomes more mobile. It was of interest to investigate an analogous reaction for mixed organosilicon acetals (Ref 2) and to explain the influence of silicon on the mobility of the oxy radical in the acetals. Different from the aliphatic-aromatic acetals the aliphatic ones easily are subjected to a symmetrization. The mixed organosilicon compounds are accompanied by a number of reactions in the symmetrization, decomposing on thermal treatment. On using the Grignard reagent with mixed organosilicon acetals the authors arrived at the conclusion that the oxy radical containing a silicon atom, is suited for substitution, independent of the fact whether it is directly connected with the oxygen or whether it is in a remote position. In either case the corresponding ethers are obtained (see scheme). Thus it was found that on the action of the Grignard reagent on the organosilicon acetals the following sequence of conversion is found:

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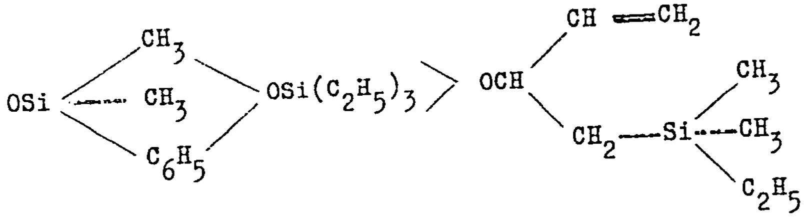
SOV/79-28-6-22/63

Investigation of the Substitution Reaction of Oxy Radicals by Radicals of Organomagnesium Compounds. III. Conversion of Organomagnesium Compounds With Mixed Organosilicon Acetals



There are 11 references, 11 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR i Azerbaydzhanskiy sel'skokhozyaystvennyy institut (Institute of Organic Chemistry, AS USSR and Azerbaydzhan Institute of Agriculture)

SUBMITTED: May 2c, 1957

Card 3/4

Investigation of the Substitution Reaction of Oxy Radicals by Radicals of Organomagnesium Compounds. III. Conversion of Organomagnesium Compounds With Mixed Organosilicon Acetals

SOV/79-28-6-22/63

1. Grignard reagents--Chemcial reactions 2. Organic acids--Chemical reactions
3. Silicon compounds (organic)--Chemical reactions

Card 4/4

SHOSTAKOVSKIY, M.F.; KULIBEKOV, M.R.

Exchange reaction of oxy and hydrocarbon radicals in magnesium organic compounds. Part 4: Interactions of the Grignarol reagent with organic acylals. Zhur.ob.khim. 28 no.9:2339-2341 S '58.
(MIRA 11:11)

1. Institut organicheskoy khimii AN SSSR i Azerbaydzhanskiy sel'skokhozyaystvennyy institut.
(Grignard reagents) (Acetic acid)

SHOSTAKOVSKIY, M.F.; GRACHEVA, Ye.P.; KUL'BOVSKAYA, N.K.

Synthesis and conversions of α-substituted vinyl ethers. Part 7: Synthesis and conversions of α-chloroisopropyl aryl ethers. Zhur. ob. khim. 28 no.9:2341-2343 S '58. (MIRA 11:11)

1. Institut organicheskoy khimii AN SSSR.
(Ethers)

SHOSTAKOVSKIY, M.F.; GRACHEVA, Ye.P.; KUL'BOVSKAYA, N.K.

Synthesis and conversions of α-substituted vinyl ethers. Part 8: Various properties of α-methylvinyl aryl and α-methylvinyl cyclohexyl ethers. Zhur.ob.khim. 28 no.9:2344-2348 S '58. (MIRA 11:11)

1. Institut organicheskoy khimii AN SSSR.
(Ethers) (Vinyl compounds)

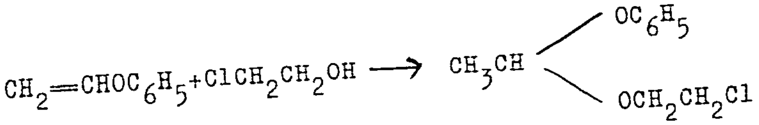
SOV/79-28-10-43/60

AUTHORS: Shostakovskiy, M. F., Kulibekov, M. R., Gorban', A. K.

TITLE: Synthesis of β-Chlorethyl-Phenyl Acetal (Sintez β-khloretilfenilatsetalya)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 10, pp 2838 - 2838 (USSR)

ABSTRACT: In previous papers (Ref 1), M.F.Shostakovskiy and his collaborators investigated the reaction of vinyl alkyl ether with ethylene chlorohydrin, as well as some chemical properties of the β-chloro-ethyl-alkyl acetals synthesized in this process. In the paper under discussion, the attachment reaction of ethylene chlorohydrin with vinylaryl ethers, starting with vinyl phenyl ether, is carried out:



$$CH_2{=}CHOC_6H_5 + ClCH_2CH_2OH \longrightarrow CH_3CH\begin{cases} OC_6H_5 \\ OCH_2CH_2Cl \end{cases}$$

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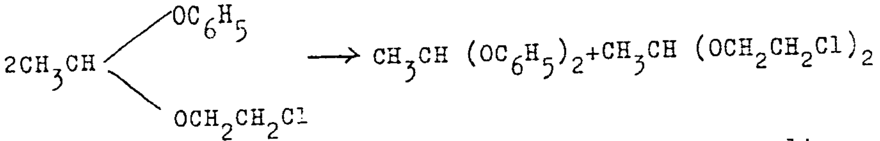
Synthesis of β-Chlorethyl-Phenyl Acetal SOV/79-28-10-43/60

On a closer study of this reaction it turned out that besides the formation of β-chloro-ethyl-phenyl acetal, its disproportionation into diphenyl acetal and β,β-dichloro-diethyl acetal occurs according to the pattern:



$$2CH_3CH\begin{matrix}OC_6H_5\\OCH_2CH_2Cl\end{matrix} \longrightarrow CH_3CH\ (OC_6H_5)_2 + CH_3CH\ (OCH_2CH_2Cl)_2$$

An analogous phenomenon could be observed on an earlier occasion in the investigation of the β-chloro-ethyl-alkyl acetals (Ref 1). This is the first time that a description of the β-chloro-ethyl-phenyl acetal is given. There are 2 references, 2 of which are Soviet.

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

SUBMITTED: July 29, 1957

Card 2/2

SOV/79-28-10-44/60

AUTHORS: Shostakovskiy, M. F., Kulibekov, M. R., Gorban', A. K.

TITLE: Synthesis of γ,γ'-Diphenyl-Dipropyl Acetal (Sintez γ,γ'-**difenildipropilatsetalya**)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 10, pp 2839 - 2839 (USSR)

ABSTRACT: In previous papers, Shostakovskiy (Ref 1) suggested a method for the synthesis of acetals of a great variety of structures, and investigated some chemical properties of these compounds. The paper under discussion served the purpose of a closer investigation of the reactions of β,β'-dichloro-diethyl acetal with Grignard's reagent. Starting from the fact that this acetal constitutes at the same time an acetal and a halogen derivative, the authors could expect that it would react either as a halogen alkyl, or, according to the Chichibabin-Yelgazin reaction pattern, at the C-O bond (Ref 2). As a result of the investigation of this reaction,

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Synthesis of γ,γ'-Diphenyl-Dipropyl Acetal SOV/79-28-10-44/60

starting with the reaction of magnesium chlorobenzyl with β,β'-dichloro diethyl acetal, it was shown that the reaction occurs, according to the following pattern, at the expense of the chlorine atoms:

$CH_3CH(OCH_2CH_2Cl)_2+2C_6H_5CH_2MgCl \rightarrow CH_3CH(OCH_2CH_2CH_2C_6H_5)_2$.

This experience runs counter to the previous investigations by the same authors (Ref 3), according to which the reaction of Grignard's reagent with symmetric and mixed acetals not containing a halogen in the alcohol radicals occurs at the C-O bond. There are 4 references, 4 of which are Soviet.

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

SUBMITTED: July 29, 1957

Card 2/2

SOV/79-28-10-45/60

AUTHORS: Shostakovskiy, M. F., Kochkin, D. A., Neterman, V. A., Sidel'kovskaya, F. P.

TITLE: Investigations in the Field of the Synthesis and Conversions of Oxygen-Containing Organosilicon Compounds (Issledovaniya v oblasti sinteza i prevrashcheniy kislorodsoderzhashchikh kremneorganicheskikh soyedineniy)
On the Reaction of Vinyl Alkyl-Chloro Silanes With Vinyl Butyl Ether and Vinyl Lactams (O vzaimodeystvii vinilalkilkhlorsilanov s vinilbutilovym efirom i vinillaktamami)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 10, pp 2840-2841 (USSR)

ABSTRACT: It is a well known fact (Refs 1, 2) that vinyl alkyl-chloro silanes do not polymerize, and that if they do, they form polymers of low molecular weights. Their polymerization, either single or together with other unsaturated compounds, suggested itself. The authors found that vinyl alkyl dihalogens polymerize neither at high temperatures (100°, 200 hours), nor with catalysts. On the other hand, the unsaturated organosilicon compounds with a double bond in the middle of the

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SOV/79-28-10-45/60

Investigations in the Field of the Synthesis and Conversions of Oxygen-Containing Organosilicon Compounds. On the Reaction of Vinyl Alkyl-Chloro Silanes With Vinyl Butyl Ether and Vinyl Lactams

silicon-carbon chain or with two conjugated double bonds tend to polymerization, either with the action of initiators or of light. Thus ethyl-dichloro butadiene silane $C_2H_5SiCl_2CH=$ $=CHCH=CH_2$ was changed, with the action of light, into a transparent, caoutchouc-like mass, within five months. At room temperatures and at 60°, no joint polymerization of the vinyl alkyl-chlorosilanes could be observed in the joint reaction of the vinyl methyl- and vinyl ethyl-dichloro silane pairs with vinyl butyl ether, vinyl caprolactam, and vinyl pyrrolidone, in the presence of azoisobutyro nitrile. In this case, the vinyl alkyl-chloro silanes act as initiators of the polymerization of vinyl butyl ether, vinyl caprolactam, and vinyl pyrrolidone. However, in the case of a reaction of vinyl alkyl-dichloro silanes with vinyl pyrrolidone, a small quantity of products containing silicon and nitrogen and probably constituting products of the reaction of these monomers, were obtained in addition to its polymers. Thus the monomer pairs do not, in effect, form a joint polymer. The polymers of vinyl

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SOV/79-28-10-45/60

Investigations in the Field of the Synthesis and Conversions of Oxygen-Containing Organosilicon Compounds. On the Reaction of Vinyl Alkyl-Chloro Silanes With Vinyl Butyl Ether and Vinyl Lactams

butyl ether, vinyl caprollactam, and vinyl pyrrolidone result as the main products of the reaction of the above-mentioned compounds. There are 3 references, 1 of which is Soviet.

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

SUBMITTED: August 17, 1957

Card 3/3

SOV/79-28-12-34/41

AUTHORS: Shostakovskiy, M. F., Shapiro, E. S.,
Dubrova, Ye. V.

TITLE: Synthesis of Polyfunctional Sulfur Compounds Starting From the Divinyl Ether and Hydrogen Sulfide (Sintez polifunktsional'nykh sernistykh soyedineniy na osnove divinilovogo efira i serovodoroda)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 12,
pp 3311 - 3316 (USSR)

ABSTRACT: Earlier (Refs 1-3) the authors had investigated the anomalous affiliation of hydrogen sulfide to the vinyl ethers and they found that dinitrile of the azoisobutyric acid was the most efficient of all catalysts used. In this paper the affiliation reaction of H_2S to the divinyl ether is carried out in their presence. Some other affiliation reactions to this ether are described as well: Halogenation and hydrohalogenation (Ref 4), affiliation of CCl_4 (Ref 5). On this problem there are only affiliations of H_2S to the diallyl ether and its homologs in the presence of butyl amine to be found in publications. Harman and Vaughan (Ref 6) obtained cyclic thioxanes and thiazanes besides the poly-

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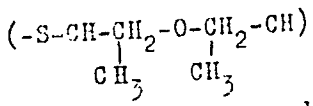
Synthesis of Polyfunctional Sulfur Compounds Starting From the Divinyl Ether and Hydrogen Sulfide

SOV/79-28-12-34/41

mers of the structure  $(-S-CH-\underset{CH_3}{\underset{|}{C}H_2}-O-\underset{CH_3}{\underset{|}{C}H_2}-CH)$ (Ref 6)

At low temperatures, increased pressure and under ultraviolet irradiation viscous products of some practical importance (Scheme 1) were obtained according to data mentioned in patents (Refs 7,8). The authors carried out the reaction of H_2S with divinyl ether in the presence of the dinitrile of azoisobutyric acid. This reaction took place stepwise under the formation of a mixture of chain-like dithiols of different composition (Scheme 2-a,b,v). The formation of compound (III) can be explained by scheme 3-a,b. The compounds (I-III) were obtained with a great excess of H_2S (Table 1). The formation of cyclic and polymeric products was not observed. Varying the conditions of the initial products sulfide dithiols could be obtained in large quantities (II, III). H_2S was used in liquid state. Thus, the dithiol and sulfide dithiol were synthesized, and it was demonstrated that these compounds have a still greater tendency to anomalous affiliation to the double bond than

Card 2/3

Synthesis of Polyfunctional Sulfur Compounds Starting From the Divinyl Ether and Hydrogen Sulfide SOV/79-28-12-34/41

thiols have. Some dithio- and trithioethers (V) were synthesized. There are 2 tables and 14 references, 9 of which are Soviet.

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

SUBMITTED: November 16, 1957

Card 3/3

SHOSTAKOVSKIY, M.F.; KOTRELEV, V.N.; KOCHKIN, D.A.; KUZNETSOVA, G.I.;
KALININA, S.P.; BORISENKO, V.V.

Synthesis and various conversions of tin and silicon organic compounds.
Zhur. prikl. khim. 31 no.9:1434-1436 S '58. (MIRA 11:10)

1. Institut organicheskoy khimii AN SSSR i Gosudarstvennyy nauchno-issledovatel'skiy i proyektnyy institut promyshlennosti plasticheskikh mass.
(Tin organic compounds) (Silicon organic compounds)

20-1-32/58

AUTHORS: Shostakovskiy, M. F., Shapiro, E. S., Shmonina, L.I.

TITLE: Chlorination of Diacetylene (Khlorirovaniye diatsetilena).
The Synthesis of Hexachlorobutadiene-1,3 (Sintez geksakhlorbutadiyena -1,3).

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr 1, pp. 114-116 (USSR).

ABSTRACT: The haloidation-reaction of diacetylene is well investigated in the example of the bromine-addition (reference 1). But there are no data on the chlorination. For this purpose the authors worked out a method: the reaction takes place in the medium of carbon tetra-chloride at -30 - 25°C. Liquid and crystalline 1,1,2,3,4,4-hexachlorobutene-2 forms. Its geometrical isomers were isolated and are known (reference 2). They are supposed not to react with chlorine and bromine. The authors, however, succeeded in performing a further chlorination of the hexachlorobutenes with liquid chlorine under pressure and ultra-violet illumination. In the case of large chlorine excess (4-8 and more Mol) they did not notice any chlorinolysis and obtained octachlorobutane with a quantitative yield. A subsequent dehydrochlorination of the latter led to the synthesis of hexachlorobutadiene-1,3. This is a substance valuable in many commercial respects. Regarding this production (references 3,4) there exist patent applications (although

Card 1/2

SHOSTAKOVSKIY, M.F.

20-3-29/59

AUTHORS: Shostakovskiy, M. F. Bogdanova, A. V., Ushakova, T. M.

TITLE: Vinyl Compounds in the Diene Synthesis (Vinilovyye soyedineniya v diyenovom sinteze). On the Diene Synthesis of Thiovinylether With Cyclopentadiene and Hexachlorocyclopentadiene (O diyenovom sinteze tiovinilovykh efirov s tsiklopentadiyenom i geksakhlortsiklopentadiyenom).

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr 3, pp. 520-522 (USSR).

ABSTRACT: In an earlier work (reference 1) the authors proved that the simple vinyl ethers ($CH_2=CH-OR$, where R is an alkyl-, aryl- or saturated hydro-aromatic radical) can take part in the diene synthesis with cyclopentadiene and hexachlorocyclopentadiene as a philodiene compound. Other facts from this field follow (references 2,3). The authors continue the systematic investigation of the syntheses mentioned in the title as the thiovinylethers now became accessible (reference 6). The first two mentioned authors (reference 8) reported a greater tendency to the reaction according to the radical mechanism of the vinyl-aryl-ethers than to that of vinyl-alkyl-ethers. The latter also occur more easily in the diene syntheses (reference

Card 1/3

Vinyl Compounds in the Diene Synthesis. On the Diene Synthesis 20-3-29/59
of Thiovinylether With Cyclopentadiene and Hexachlorocyclopentadiene.

PRESENTED: July 25, 1957, by A.V. Topchiyev, Academician

SUBMITTED: July 24, 1957

AVAILABLE: Library of Congress

Card 3/3

AUTHORS: Bogdanova, A. V., Shostakovskiy, M. F., SOV/20-120-2-20/63
Plotnikova, G. I.

TITLE: The Interaction Between Diacetylene and Ethyl Mercaptan, and Some Properties of the Compounds Obtained (Vzaimodeystviye diatsetilena s etilmerkantanom i nekotoryye svoystva poluchennykh soyedineniy)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 2, pp. 301-304 (USSR)

ABSTRACT: Several ethynyl-vinyl-ethers (References 1,3) were produced by synthesis on a diacetylene basis. They are interesting from the point of view of their reactivity and the possibility of producing 1-alcoxy-butadiene-1,3 (Reference 4). It was interesting to investigate the interaction mentioned in the title, as publications on this problem are restricted to one single patent mentioned (Reference 5). The authors obtained this interaction already on slight heating; under the influence of alkali the reaction already begins at room temperature and is accompanied by self-heating. There are

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proofs that the first stage of the interaction under review takes place according to an ionic mechanism. According to the ratio of initial substances and the temperature the reaction follows scheme (I) or is accompanied by the formation of ethynyl-vinyl-thioethyl-ether and a product of the addition of 2 mercaptan-molecules which has a butadiene-structure (scheme (II)). The interaction takes a stepwise course, as the second stage can also take place independently with another mercaptan. The addition of mercaptan to the ethynyl-vinyl-thioethyl-ether may take place under the influence of different reagents (alkali, HCl, radical-initiators and heating). In the last 2 cases the yields of the final product are higher. Thus this addition reaction takes place more advantageously according to a radical mechanism than according to an ionic mechanism. The chief products in this connection are dithio-alkyl-butadiene-1,3. A certain difference of the physical constants and a strong exaltation of the molecular refraction of the addition product of 2 mercaptan-molecules to diacetylene is apparently explained by the presence of 2 isomeric compounds, others than those with a butadiene-structure also being possible among them. Ethynyl-vinyl-thioethyl-ether reacts with a sublimate solution in alcohol and quantitatively forms ethyl-mercapto-mercury-chloride, an equivalent amount of HCl and apparently ethyl-vinyl-ethyl-ether. Thus this method can be employed for the determination of ethynyl-vinyl-thio-alkyl-ethers. In a kind of experimental part details of the reactions, constants and yields are described under conditions of: a) interaction of diacetylene with ethyl-mercaptan; b) decomposition of ethynyl-vinyl-ether and the product with 2 mercapto -groups by sublimate solution in alcohol (table 2); c) hydrolysis of the latter ether and the 2-mercapto-group product in the presence of sublimate (table 3); d) interaction of ethynyl-vinyl-thioethyl-ether with ethyl-mercaptan and thiophenol (table 4); e) condensation with maleic anhydride.

The Interaction Between Diacetylene and Ethyl Mercaptan, and Some Properties of the Compounds Obtained SOV/20-120-2-20/63

There are 4 tables and 9 references, 7 of which are Soviet.

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

PRESENTED: January 8, 1958, by B. A. Kazanskiy, Member, Academy of Sciences, USSR

SUBMITTED: January 7, 1958

1. Acetylenes--Chemical reactions 2. Thiols--Chemical reactions 3. Ethers--Synthesis 4. Cyclic compounds--Properties

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IONIDI, Perikl Petrovich; SHOSTAKOVSKIY, M.F., doktor khimicheskikh nauk,
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[D.I.Mendeleev's world outlook] Mirovozzrenie D.I.Mendeleeva.
Moskva, Izd-vo Akad.nauk SSSR, 1959. 374 p. (MIRA 13:1)
(Mendeleev, Dmitrii Ivanovich, 1834-1907)

Shostakovskiy, M.F.

11(4) PHASE I BOOK EXPLOITATION SOV/2075

Akademiya nauk SSSR. Bashkirskiy filial, Ufa

Khimiya seraorganicheskikh soyedineniy, soderzhashchikhsya v neftyakh i nefteproduktakh; [materialy III nauchnoy sessii] (Chemistry of Sulphur Organic Compounds Contained in Petroleum and Petroleum Products; [Papers of the Third Scientific Session]) Moscow, Izd-vo AN SSSR, 1959. 376 p. 2,000 copies printed. Errata slip inserted.

Editorial Board: R.D. Obolentsev (Resp. Ed.) Doctor of Chemical Sciences; G.D. Gal'pern, Doctor of Chemical Sciences; Ya. B. Chertkov, Doctor of Technical Sciences; V.V. Panov, Candidate of Technical Sciences; and V.P. Rozhdestvenskiy, Candidate of Chemical Sciences; Ed. of Publishing House: I.I. Brusov; Tech. Ed.: T.P. Polenova.

PURPOSE: This book is intended for chemists, chemical engineers, and technicians specializing in the chemistry of petroleum.

COVERAGE: The book is a collection of papers presented at the Third Scientific Session on the Chemistry of Organic Sulfur- and Nitrogen Compounds Contained in Petroleum and Petroleum Products. The scientific session was held in Ufa, June 3-8, 1957. The book consists of six sections: 1) Synthesis, characterization, and analysis of organic sulfur compounds; 2) Separation and composition of organic sulfur compounds contained in petroleum and petroleum products; 3) Transformation of organic sulfur compounds by thermal catalysis; 4) Corrosive properties of and tar formation in sulfur-containing petroleum and petroleum products; 5) Uses of organic sulfur compounds and hydrogen sulfide; 6) Physiological properties of organic sulfur compounds. No personalities are mentioned. There are 315 references, of which 179 are Soviet, 118 English, 5 French, 12 German, and 1 Czech.

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Chemistry of Sulphur Organic Compounds (Cont.) SOV/2075

PART V. USES OF ORGANIC SULFUR COMPOUNDS

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SOV/62-59-1-21/38

5(3)

AUTHORS: Shostakovskiy, M. F., Chekulayeva, I. A.

TITLE: Synthesis and Transformations of Vinyl Ethers of Ethanol Amines (Sintez i prevrashcheniya vinilovykh efirov etanolaminov). Communication 10. Free-radical Polymerization and Copolymerization of Trivinyl Ether of Triethanol Amine (Soobshcheniye 10. Svobodnoradikal'naya polimerizatsiya i sopolimerizatsiya trivinilovogo efira trietanolamina)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 130 - 133 (USSR)

ABSTRACT: In the present paper the authors investigated the polymerization of trivinyl ethers of triethanol amine $(CH_2=CHOCH_2CH_2)_3N$ and its copolymerization with methyl methacrylate under the influence of benzoyl peroxide and dinitrile of the azoisobutyric acid and determined some laws governing this reaction. The results of the investigations are given (Tables 1 and 2). It was found that the polymerization of the respective vinyl ether and its copolymerization with methyl methacrylate are not initiated by benzoyl peroxide. The polymerization and copolymerization of trivinyl ethers of triethanol amine with methyl methacrylate was carried out in the presence of dinitrile of azobutyric acid. It was

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Synthesis and Transformations of Vinyl Ethers of Ethanol SOV/62-59-1-21/38
Amines. Communication 10. Free-radical Polymerization and Copolymerization
of Trivinyl Ether of Triethanol Amine

stated that primarily three-dimensional products are produced therein. Polymers and copolymers were hydrolized with sulfuric acid of 2% at 20°. The authors found that they contain free vinyl groups. The products of hydrolysis possess also a three-dimensional structure. The results of the hydrolysis are presented in table 3. There are 1 figure, 3 tables and 7 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 18, 1957

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SOV/62-59-1-22/38

5(3)

AUTHORS: Shostakovskiy, M. F., Gladyshevskaya, V. A., Chekulayeva, I. A.

TITLE: Synthesis and Transformations of Vinyl Ethers of Ethanol-Amines (Sintez i prevrashcheniya vinilovykh efirov etanolaminov) Communication 11. Some Features of Copolymerization of Vinyl Ethers of the β-Aminoethanol and Methyl Esters of Methacrylic Acid (Soobshcheniye 11. Ob osobennostyakh sopolimerizatsii vinilovogo efira β-aminoetanola i metilovogo efira metakrilovoy kisloty)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 134 - 139 (USSR)

ABSTRACT: Since the dinitrile of the azoisobutyric acid, unlike benzoyl peroxide, includes not only methyl methacrylate but also the vinyl ether of β-aminoethanol in the polymerization (Ref 2) the authors investigated the copolymerization of these substances under the effect of dinitrile of the azoisobutyric acid. It was shown that the interaction of the components mentioned is complicated. Apparently three compounds participate in the copolymerization: vinyl ether

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Synthesis and Transformations of Vinyl Ethers of Ethanol Amines. Communication 11. Some Features of Copolymerization of Vinyl Ethers of the β-Aminoethanol and Methyl Esters of Methacrylic Acid SOV/62-59-1-22/38

of β-aminoethanol, methyl methacrylate and the product of their interaction, i. e. the methyl ester of β-(β-vinyl oxy-ethyl) aminoisobutyric acid. The latter is formed according to the equation

$$CH_2=CHOCH_2CHNH_2+CH_2=C(CH_3)COOCH_3 \rightarrow$$

$$\rightarrow CH_2=CHOCH_2CH_2NHCH_2CH(CH_3)COOCH_3$$

during the reaction so that its concentration in the system remains unknown. The participation of the three components in the copolymerization leads to the formation of 2 fractions of the copolymer for each ratio of the initial monomers (Table 1). The process investigated is complicated by the fact that besides copolymerization and addition also condensation takes place. This is a result of the fact that besides multiple bonds also other functional groups of the initial components participate in the reaction, which leads to the formation of copolymers with three-dimensional structure. In addition, the polymerization of methyl ester of β-(β-vinyl oxy-ethyl)aminoisobutyric acid and its copolymeriza-

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Synthesis and Transformations of Vinyl Ethers of Ethanol SOV/62-59-1-22/38
Amines. Communication 11. Some Features of Copolymerization of Vinyl Ethers
of the β-Aminoethanol and Methyl Esters of Methacrylic Acid

tion with methyl methacrylate under the influence of dinitrile of azoisobutyric acid (Table 3) were carried out. There are 3 tables and 6 references, 2 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 6, 1957

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5(3)

SOV/62-59-2-21/40

AUTHORS:	Shostakovskiy, M. F., Bogdanova, A. V., Krasil'nikova, G. K.
TITLE:	Investigation in the Field of Diacetylene Derivatives (Issledovaniye v oblasti proizvodnykh diatsetilena). Communication 2. Some Transformations of Alkoxy-butanes and Preparation of 1-Alkoxy-butadienes-1,3 (Soobshcheniye 2. Nekotoryye prevrashcheniya alkoksibutanov i polucheniye 1-alkoksi-butadiyenov-1,3)
PERIODICAL:	Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1959, Nr 2, pp 320-326 (USSR)
ABSTRACT:	In the present paper the decomposition of the 1,1,3-trioxy-butanes synthesized by the authors and some transformations of products of their thermal decomposition were investigated and a method of synthesis of alkoxy-butadienes-1,3 suggested. A noticeable thermal decomposition of trioxybutane begins at ~200°, butyl alcohol, 1,3-dibutoxy butene-1 (IV), its dimer and the partly polymerizing 1-butoxy butadiene-1,3 (I) being separated. 1-butoxy butadiene-1,3 (I) was also obtained on the thermal decomposition of (IV) which indicates a gradual proceeding of the reaction. 1,3-dibutoxy butene (IV) obtained on the

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Investigation in the Field of Diacetylene Derivatives. Communication 2. Some Transformations of Alkoxy-butanes and Preparation of 1-Alkoxy-butadienes-1,3

decomposition of tributoxy butane may be regarded as a β-substituted vinyl ehter. It really displaces some properties of vinyl ether. On its hydrolysis the alkoxy group in the γ position is split off and vinyl acetaldehyde (VI) formed, it reacts intensely with gaseous hydrogen chloride and forms α-chloro-γ-butoxy-dibutyl ether (VII). On hydrogenation of 1,3-dibutoxy-butene-1 under usual conditions alcohol is split off, but no dibutoxy-butane is formed. On condensation of 1-cyclohexoxy-butadiene-1,3 (II) with maleic acid anhydride the copolymerization of the anhydride with butadiene took place in addition to the formation of an adduct. An apparently regularly built polymer was separated therein. By means of condensation of 1-alkoxy-butadiene-1,3 with croton aldehyde methyl-alkoxy-tetrahydrobenzaldehyde was obtained. In addition to the thermal decomposition of 1,1,3-trialkoxy-butanes the hydrolytic cleavage of these compounds was investigated. On the hydrolysis of 1,1,3-tributoxy-butane (X) and 1,1-dibutoxy-3-phenoxy-butane (XI) 3-butoxy-butanal (XII) and 3-phenoxy-butanal (XIII) were separated. It was found that the hydrolysis on permanent heating is

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Investigation in the Field of Diacetylene Derivatives. Communication 2. Some Transformations of Alkoxy-butanes and Preparation of 1-Alkoxy-butadienes-1,3

accompanied by separation of the alcohol molecule and the formation of vinyl acetaldehyde (XIV). This indicates that in the aldehyde the formation of the alkoxy group in β position is not stable as compared with trialkoxy-butane. In the latter this group is split off only on continuous heating up to 220°. There are 12 references, 4 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 31, 1957

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Investigation in the Field of Lactones and Lactams. SOV/62-59-3-20/37
Communication 13. Alkoxyethylidene-pyrrolidones

An increase in temperature up to 85° provides a good yield of ethylidene-bis-N-N'-pyrrolidone (Experiments 6,10). Experiment 2 shows optimum conditions for the formation of butoxyethylidene pyrrolidone and experiment 9 for the formation of isopropoxyethylidene pyrrolidone. The most comfortable method of synthesis of alkoxyethylidene pyrrolidones as well as of alkoxyethylidene caprolactams is the interaction of α-chloroethylalkylethers with lactams. This reaction, however, exhibits a number of peculiar features for pyrrolidone. The yield of alkoxyethylidene pyrrolidones, for instance, is small, further, in addition to them ethylidene-bis-N-N'-pyrrolidone is always formed. Certain differences may be observed also on the thermal decomposition of these two compounds. On thermal decomposition of alkoxyethylidene caprolactams vinylcaprolactam is obtained in high yield (70-80 %). On the other hand it is not always possible to obtain vinylpyrrolidone on decomposition of alkoxyethylidene pyrrolidones. On decomposition of butoxyethylidene pyrrolidone vinylpyrrolidone in a $\sim$40 % yield and butanol were obtained. On decomposition of isopropoxyethylidene-pyrrolidone isopropyl alcohol, pyrrolidone, and ethylidene-

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Investigation in the Field of Lactones and Lactams. SOV/62-59-3-20/37
Communication 13. Alkoxyethylidene-pyrrolidones

-bis-N-N'-pyrrolidone were separated. The thermal decomposition of ethylidene-bis-N-N'-pyrrolidone takes place at considerably higher temperature than the decomposition of alkoxyethylidene lactams. As result of this decomposition pyrrolidone and a resinous residue were separated. There are 1 table and 8 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: June 21, 1957

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5(3) SOV/62-59-4-29/42

AUTHORS: Shostakovskiy, M. F., Sidel'kovskaya, F. P., Zelenskaya, M. G.

TITLE: Reaction of Propylene Oxide With α-Pyrrolidone (Reaktsiya okisi propilena s α-pirrolidonom)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 738-740 (USSR)

ABSTRACT: This is a brief report on the investigation of the reaction of α-pyrrolidone with propylene oxide. In this case the oxide ring opens in a way so that a secondary alcohol is formed:

$$CH_3\overline{CHCH_2O} + \overline{NHCO(CH_2)_3} \longrightarrow CH_3CH(OH)CH_2\overline{NCO(CH_2)_3}$$

The structure of the N-(β-oxypropyl)α-pyrrolidone obtained was proved by the synthesis of γ-butyrolactone and aminoisopropanol. The aminoisopropanol required was obtained from ammonia and propylene oxide (Ref 3). Upon interaction of N-(β-oxypropyl)α-pyrrolidone with thionyl chloride the hydroxyl group was substituted by chlorine and N-(β-chloropropyl)α-pyrrolidone obtained. Upon heating with aqueous alkali this chloride is hydrolyzed (Table),

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Reaction of Propylene Oxide With α-Pyrrolidone SOV/62-59-4-29/42

although, more slowly than the N-(chloromethyl) α-pyrrolidone obtained earlier (Ref 4) which saponifies quantitatively at room temperature even in the absence of alkali. Upon heating of N-(β-chloropropyl) α-pyrrolidone with caustic potash in benzene solution, HCl was separated and N-(propenyl) α-pyrrolidone formed. The position of the double bond was determined by spectroscopy. This investigation was carried out by T. N. Shkurina. There are 1 table and 6 references, 3 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: July 24, 1958

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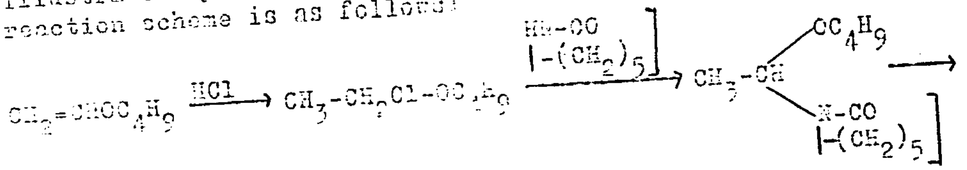
5 (3) SOV/62-59-5-19/40

AUTHORS: Shostakovskiy, M. F., Sidel'kovskaya,
F. P.

TITLE: Investigation in the Field of Lactones and Lactams
(Issledovaniye v oblasti laktonov i laktamov). Communication
14. Synthesis of Vinylcaprolactam by the Method of Indirect
Vinylation (Soobshcheniye 14. Sintez vinilkaprolaktama
metodom kosvennogo vinilirovaniya)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 5, pp 892-895 (USSR)

ABSTRACT: In a previous work the authors found that alkoxyethylidenelactams can be used in the indirect introduction of the vinyl group into the lactam molecule. The course of the reaction is illustrated by the example of butoxyethylenecaprolactam. The reaction scheme is as follows:



$$CH_2=CHOC_4H_9 \xrightarrow{HCl} CH_3-CH_2Cl-OC_4H_9 \xrightarrow{\overset{HN-CO}{\lfloor -(CH_2)_5 \rfloor}} CH_3-CH\begin{cases} OC_4H_9 \\ N-CO \\ \lfloor -(CH_2)_5 \rfloor \end{cases} \longrightarrow$$

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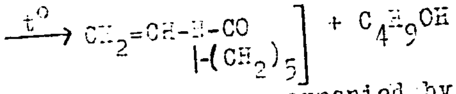
SOV/62-59-5-19/40

Investigation in the Field of Lactones and Lactams. Communication 11. Synthesis of Vinylcaprolactam by the Method of Indirect Vinylation



$$\xrightarrow{t^{0}} CH_2=CH-N-CO \Big|-(CH_2)_5\Big] + C_4H_9OH$$

The process is accompanied by thermopolymerization of lactam by which the monomer yield of this compound is considerably reduced. This paper gives a detailed investigation of the thermal decomposition of alkoxyethylidenecaprolactams in order to improve the conditions of synthesis of the indirect vinylation method. Butoxy-, ethoxy-, and isopropoxyethylidenecaprolactam were used as examples in the investigation of the reactions. Caprolactam and α-chloroethylisopropyl ether were the initial products of the synthesis. The highest yield was obtained when the two substances showed a ratio of 1 : 2. Thermal decomposition was investigated at 200-280°. At the same time the corresponding alcohols and vinylcaprolactams are formed. The yield of vinylcaprolactam increases if the decomposition takes place in the presence of 1 % hydroquinone; it then amounts to 80 %. If

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Investigation in the Field of Lactones and Lactams. SOV/62-58-3-[illegible]
Communication 14. Synthesis of Vinylcaprolactam by the Method of Indirect Vinylation

alkoxyethylidenelactams are heated in the presence of small quantities of concentrated hydrochloric acid they undergo partial hydrolysis. The syntheses and methods of investigation are described in detail in the experimental part. There are 1 table and 6 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: July 18, 1957

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5 (3)

SOV/62-59-5-20/40

AUTHORS: Shostakovskiy, M. F., Vasil'yev, A. [illegible], Zelenskaya, [illegible] G., Sidel'kovskaya, F. P., Morgunova, Ye. S., Gyul'badamova, N. N.

TITLE: Investigation in the Field of Lactones and Lactams (Issledovaniye v oblasti laktonov i laktamov). Communication 15. Preparations of Polyvinylpyrrolidones Having Different Molecular Weights and Their Physico-chemical Properties (Soobshcheniye 15. Preparaty polivinilpirrolidona razlichnogo molekulyarnogo vesa i ikh fizikokhimicheskiye svoystva)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 5, pp 896-900 (USSR)

ABSTRACT: "Block polymerization" of vinylpyrrolidone under the effect of H_2O_2 and of dinitrile of azoisoolsic acid, and polymerization in aqueous solutions (Refs 3, 5) had been investigated at the Institute mentioned under Association. In connection with it, the physico-chemical properties of various preparations of polyvinylpyrrolidone (PVP) were investigated in this work because these properties are very important for the investigation of the biologic activity of the preparations.

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SOV/62-59-5-20/40

Investigation in the Field of Lactones and Lactams. Communication 15. Preparations of Polyvinylpyrrolidones Having Different Molecular Weights and Their Physico-chemical Properties

The preparations can be obtained in various ways; therefore, they may exhibit slight deviations from their physico-chemical characteristics. (Table 1: physico-chemical characteristics of (PVP) solutions as produced in various countries). The polymerization conditions for (PVP) from aqueous solutions in the presence of 30 % H_2O_2 and with 0.8-8.5 % concentrations of this initiator are summarized in table 2. The characteristics of salt water solutions of (PVP) being used as a plasmosubstitute are shown in table 3. Relative viscosity, osmotic pressure, and the molecular weight of the various preparations were determined. A comparison of the characteristics shows that those of (PVP) are more effective than those of the plasmosubstitute. 1.8 % H_2O_2 had to be used as initiator in order to obtain a highly effective polymer. The determination of the molecular weight and the investigation of the polydispersity of several preparations showed that the block polymers have a higher degree of polydispersity than those obtained in solutions. Moreover,

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Investigation in the Field of Lactones and Lactams. SOV/62-59-5-20/40
Communication 15. Preparations of Polyvinylpyrrolidones Having Different
Molecular Weights and Their Physico-chemical Properties

a method for obtaining biologically active sterile salt water solutions of the preparations has been worked out. There are 2 figures, 4 tables, and 21 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: July 18, 1957

Card [illegible]

5(3)

AUTHORS: Sidel'kovskaya, F. P., Zelenskaya, M. G., SOV/62-59-5-21/40
Shostakovskiy, M. F.

TITLE: Investigation in the Field of Lactones and Lactames (Issledovaniye v oblasti laktonov i laktamov). Report 16. N-Methylol-lactames (Soobshcheniye 16. N-Metilollaktamy)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 5, pp 901-903 (USSR)

ABSTRACT: In this paper the synthesis of N-methylol-lactames of the following structure was investigated: Methylol pyrrolidone (I) $\overline{(CH_2)_3CON}CH_2OH$ and N-methylol caprolactame (II) $\overline{(CH_2)_5CON}CH_2OH$, and some of their properties were determined. The authors of the present paper showed in a previous one that in the case of an action of a 30 % formaldehyde solution upon pyrrolidone and caprolactame the following is produced in an alkali medium with a yield of 70 - 90 % (I) and (II):

$$\overline{(CH_2)_n\ CONH} + CH_2O \xrightarrow{OH^-} \overline{(CH_2)_n\ CON}CH_2OH \text{ (Ref 3).}$$

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Investigation in the Field of Lactones and Lactames . SOV/62-59-5-21/40
Report 16. N-Methylol-lactames

This scheme is to be proved. For this purpose, the reaction of these compounds with thionylchloride

$$OHCH_2\underline{N(CH_2)_nCO} + SOCl_2 \longrightarrow ClCH_2\overline{NCO(CH_2)_n} + HCl + SO_2$$

was investigated, and the compounds N-chloromethyl pyrrolidine and N-chloromethyl caprolactame were obtained with a yield of ~80 %. The chlorine content of these compounds was determined by titration according to the method developed by Volhardt (table), and it was shown that the chlorine atom in these compounds is easily saponified. Both synthesis and investigation are described separately in the experimental. There are 1 table and 6 references, 2 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: July 26, 1957

Card 2/2

5(3)

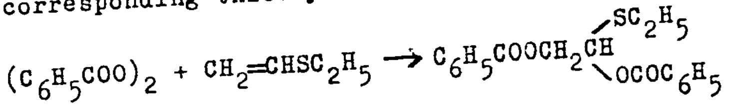
AUTHORS: Shostakovskiy, M. F., Prilezhayeva, Ye. N., Gershteyn, N. A., Karavayeva, V. M.

SOV/62-59-5-22/40

TITLE: The Synthesis of Sulfurous Substances on the Basis of Vinyl Ethers and Acetylene (Sintez sernistykh veshchestv na osnove vinilovykh efirov i atsetilena). Report 22. On the Reaction of Vinyl-ethyl Sulfide With Benzoyl Peroxide (Soobshcheniye 22. O reaktsii viniletilsul'fida s perekis'yu benzoila)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 5, pp 904-909 (USSR)

ABSTRACT: The reaction mentioned in the subtitle is investigated. It develops strictly exothermically and begins without previous heating, the reaction product being formed practically completely from the initial product: The corresponding thioacylal (1-ethylmercapto-1.2 dibenzoate ethane)



$$(C_6H_5COO)_2 + CH_2{=}CHSC_2H_5 \rightarrow C_6H_5COOCH_2CH\genfrac{}{}{0pt}{}{SC_2H_5}{OCOC_6H_5}$$

The character of the reaction products is shown by table 1.

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The Synthesis of Sulfurous Substances on the Basis of Vinyl Ethers and Acetylene. Report 22. On the Reaction of Vinyl-ethyl Sulfide With Benzoyl Peroxide

SOV/62-59-5-22/40

The reaction is so rapid that no polymerization of the vinyl-ethyl sulfide cannot take place. The benzoyl peroxide can therefore not be used as initiator for this polymerization. The simple radical may, however, lead to a slow low polymerization of the vinyl sulfide (system of equations 2 - 7) which develops in form of a chain reaction. Furthermore, it was possible to carry out polymerization with ditertiary butyl peroxide also with formation of low-molecular polymers. It was, however, not possible to obtain affiliation products. In the experimental the individual syntheses and reactions are described. There are 2 tables and 14 references, 7 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: July 30, 1957

Card 2/2

5 (3)

AUTHORS: Shostakovskiy, M. F., Kondrat'yev, Kh. I. SOV/62-59-6-15/36

TITLE: Investigations in the Field of Synthesis and Transformations of Oxygen Containing Silicon Organic Compounds (Issledovaniye v oblasti sinteza i prevrashcheniy kislorodsoderzhashchikh kremneorganicheskikh soyedineniy). Communication 8. Synthesis and Study of the Properties of Low Molecular Ethers of the Methyl-α-naphthylsilandiol (Soobshcheniye 8. Sintez i izucheniye svoystv nizkomolekulyarnykh efirov metil-α-naftilsilandiola)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 1041 - 1048 (USSR)

ABSTRACT: The different possibilities of synthesizing the derivatives of the compound mentioned in the first title, which are well known from publications, are dealt with in brief (Refs 1-11). The synthesis carried out by the authors is based upon a possible analogous reaction (Ref 14) between alcohols and silanols (Refs 12,13 polysilicon acid with alcohols), and is carried out by reaction between silandiols and alcohols, which was not yet described in publications. This reaction is of both theoretical and practical interest. As the aromatic silandiols are only weakly acid, they react with alcohol without catalysts. This

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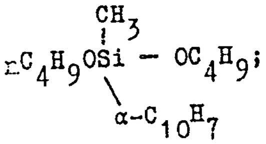
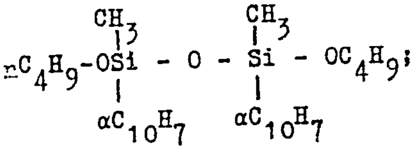
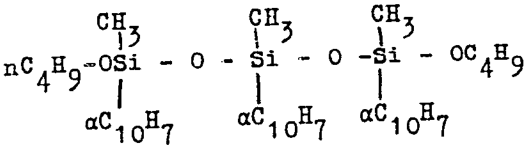
Investigations in the Field of Synthesis and Transformations of Oxygen Containing Silicon Organic Compounds. Communication 8. Synthesis and Study of the Properties of Low Molecular Ethers of the Methyl-α-naphthylsilandiol SOV/62-59-6-15/36

property was investigated with the compounds mentioned in the title and buthylalcohols. The following was obtained simultaneously: dibuthylether of the methyl-α-naphthylsilandiol (I), dibuthylether of disiloxane (II), dibuthylether of trisiloxane (III), and an imperfect buthyl ether of tetrasiloxane (IV):

I)

$nC_4H_9OSi(CH_3)(\alpha\text{-}C_{10}H_7) - OC_4H_9$;

II

$nC_4H_9\text{-}OSi(CH_3)(\alpha C_{10}H_7) - O - Si(CH_3)(\alpha C_{10}H_7) - OC_4H_9$;

III

$nC_4H_9\text{-}OSi(CH_3)(\alpha C_{10}H_7) - O - Si(CH_3)(\alpha C_{10}H_7) - O - Si(CH_3)(\alpha C_{10}H_7) - OC_4H_9$

Card 2/3 IV containing another more Si-O.

Investigations in the Field of Synthesis and Transformations of Oxygen Containing Silicon Organic Compounds. Communication 8. Synthesis and Study of the Properties of Low Molecular Ethers of the Methyl-α-naphthylsilandiol SOV/62-59-6-15/36

The reaction scheme is given. The yield in the compounds mentioned depends upon temperature, mixing intensity, the ratio of initial components, reaction time, and upon the pressure applied. Thus, it is of considerable importance with respect to the yield that the synthesis of di-n-buthylether is carried out in a vacuum. The syntheses are described in detail in the experimental part. The results obtained within the course of the synthesis (separation of the products and determination) are given in tables 1 and 3. Table 2 contains the physical characteristics of the different substances that were synthetized. There are 3 tables and 15 references, 8 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: August 5, 1957

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5 (3)

AUTHORS: Shostakovskiy, M. F., Bogdanova, A. V., Plotnikova, G. I.

SOV/62-59-8-35/42

TITLE: Letter to the Editor

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 8, p 1505 (USSR)

ABSTRACT: The authors state in this letter to the editor that they were able to synthesize the bis-thiobutadiene into disulfones while preserving the diene structure, starting from the synthesis (Ref 2) for the first time carried out by them of bis(alkylthio)- and bis(arylthio)-butadiene:

$C_6H_5SCH{=}CH{-}CH{=}CH{-}SC_6H_5$ (I) $C_6H_5S(O_2)CH{=}CH{-}CH{=}CH(O_2)SC_6H_5$ (II)

$\xrightarrow{H_2O_2}$

$C_2H_5SCH{=}CH{-}CH{=}CH{-}SC_2H_5$ (III) $C_2H_5S(O_2)CH{=}CH{-}CH{=}CH(O_2)SC_2H_5$ (IV)

Physical data and elementary composition of the two compounds are given. There are 3 references, 2 of which are Soviet.

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Letter to the Editor SOV/62-59-8-35/42

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

SUBMITTED: May 7, 1959

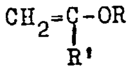
Card 2/2

5 (3)

AUTHORS: Shostakovskiy, M. F., Mamedov, Mageram SOV/62-59-9-19/40

TITLE: Investigations of Vinyl-substituted Ethers. Communication 1. Synthesis of α-Substituted Vinyl Ethyl Ethers

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, pp 1636 - 1639 (USSR)

ABSTRACT: There are two courses of synthesis for vinyl ether of the general structure of  $CH_2=\underset{R'}{C}-OR$ (R,R' = alkyl of the aryl)

a) condensation of the alcohols with alkyl acetylene, b) by separation of HBr from β-bromo alkyl ether. The following Soviet authors are mentioned in the course of discussing the appropriate publications: Favorskiy (Ref 1), Shostakovskiy and Gracheva (Ref 2), Petrov (Ref 9), Isagulyants and Maksimova (Ref 10). In the present paper the authors followed the second method and worked according to the following scheme:

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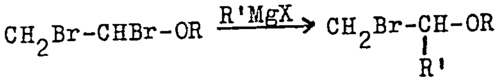
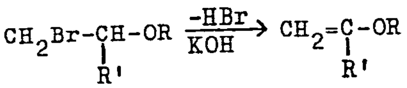
Investigations of Vinyl-substituted Ethers. Communication 1. SOV/62-59-9-19/40
Synthesis of α-Substituted Vinyl Ethyl Ethers

$$CH_2{=}CH{-}OR \xrightarrow{Br_2} CH_2Br{-}CHBr{-}OR \qquad (1)$$


(2)

$$CH_2Br{-}CHBr{-}OR \xrightarrow{R'MgX} CH_2Br{-}\underset{\displaystyle R'}{\underset{|}{C}}H{-}OR \qquad (2)$$


(3)

$$CH_2Br{-}\underset{\displaystyle R'}{\underset{|}{C}}H{-}OR \xrightarrow[KOH]{-HBr} CH_2{=}\underset{\displaystyle R'}{\underset{|}{C}}{-}OR \qquad (3)$$

Nesmeyanov, Lutsenko, Vereshchagina (Ref 11) also obtained α-methyl vinylbutyl ether according to this scheme. The warming-up rate had a large influence on the reaction. The separation of HBr improved with slower heating. For the first time they obtained β-bromine-α-ethyl diethyl-ether, α-propylvinyl ethyl ether and α-isoamyl vinylethyl ether. The structure was proved. There are 1 table and 13 references, 7 of which are Soviet.

Investigations of Vinyl-substituted Ethers. Communication 1. SOV/62-59-9-19/40
Synthesis of α-Substituted Vinyl Ethyl Ethers

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

SUBMITTED: December 27, 1957

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SOV/62-59-9-36/40

5(3)

AUTHORS: Shostakovskiy, M. F., Chekulayeva, I. A., Kondrat'yeva, L. V.

TITLE: Interaction Between Diacetylene and Amines

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, p 1690 (USSR)

ABSTRACT:

The authors report an addition of amines and diamines to diacetylene, by means of which various nitrogen containing unsaturated compounds were also obtained in good yields without use of a catalyst. Hitherto, compounds of this kind were mentioned once only in patent publications (Ref 2), for the synthesis of which catalysts were applied. Primary amines form N-alkyldiamino-1,4(-1,3)-butadiene-1,3 (Yield 80%) with diacetylene. Secondary amines form N,N-dialkylamino-1-buten-1-ine-3 (Yield 60%) with diacetylene. By addition of a second molecule of amine, these compounds give 1,4-diaminobutadienes. Diacetylenes can also add diamines, giving compounds of various structures according to reaction conditions. The structures of these compounds were

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Interaction Between Diacetylene and Amines SOV/62-59-9-36/40

confirmed by means of hydrolysis, diene synthesis, and spectroscopy. There are 2 references, 1 of which is 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 6, 1959

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77081
SOV/62-59-12-25/43

5 3-00

AUTHORS: Shostakovskiy, M. F., Gladyshevskaya, V. A., Baykova, R. I.

TITLE: Viscosity Constant for Vinyl Ether Polymers

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk 1959, Nr 12, pp 2204-2207 (USSR)

ABSTRACT: Staudinger's equation $\eta_{sp}/C = K_m M$ allows one to determine the viscosity constant only in the molecular weight range from 500 to 50,000. High-molecular-weight compounds consisting of a mixture of polymeric homologs give on fractionation narrow polymer fractions but not individual polymers, and this influences the value of K_m obtained with this equation for polymers above 50,000 molecular weight. The authors suggested therefore a method for determining the viscosity of poly(vinyl alkyl ethers) based on the study of low-molecular (di-, tri-, tetramer, etc.) compounds obtained in the multistep synthesis previously described (this journal, 1955, p 140; ibid., p 344) such as, -1,1,3-triethoxybutane-1,1,3,5-tetra-

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Viscosity Constant for Vinyl Ether Polymers

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ethoxyhexane, etc., etc. This method allows one to establish the most exact relationship between structure, composition, viscosity, and molecular weight of polymers.

The viscosity and $K_m \cdot 10^4$ of individual compounds and, for comparative purposes, those of the corresponding ether fractions, were determined and tabulated. The following were investigated: 10% solutions of 1,1,3-triethoxybutane; 1,1,3,5-tetraethoxyhexane; 1,1,3,5,7-pentaethoxyoctane; 1,1,3,5,7,9-hexaethoxydecane; 1,1,3,5,7,9,11-heptaethoxydodecane; and 1% solutions of poly(vinyl ethyl ether) fractions (in acetone, heptane, and CCl_4); 10% solutions of 1,1,3-triisopropoxybutane; 1,1,3,5-tetraisopropoxyhexane; 1,1,3,5,7-pentaisopropoxyoctane (in acetone and heptane); 1,1,3-tributoxybutane; 1,1,3,5-tetrabutoxyhexane; 1,1,3,5,7-pentabutoxyoctane; and 1% solutions of poly (vinyl butyl ether) (in acetone, heptane, and CCl_4).

It was found that there was no bond formation between the molecules of the investigated compounds and solvents, as evidenced by the time of outflow of the solutions

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Viscosity Constant for Vinyl Ether Polymers

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which was governed in all cases by a definite rule, and as evidenced by the coinciding values of the viscosity constants for the individual alkoxy compounds and fractions of a given vinyl alkyl ether. The only deviation was observed in triethoxybutane (dimer) and tetraethoxyhexane (trimer) caused probably by the influence of the terminal group. The mechanism of vinyl ether polymerization, and the influence of the chemical structure of the polymers alkoxy groups on the viscosity constant K_m is discussed. Generally speaking, the constant increases with increasing radical size of the alkoxy group. There are 9 tables; and 8 references, 1 U.S., 1 Swiss, 6 Soviet. The U.S. reference is: R. Fordlyce, H. Hibbert, J. Amer. Chem. Soc., 61, 1912 (1939). Abstracter's Note: Staudinger's equation appears in the article also in the form: $\eta_{sp}/c = K_m M$.

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

SUBMITTED: April 15, 1958

Card 3/3

77082
SOV/62-59-12-26/43

5.3610,5.3100

AUTHORS: Shorygin, P. P., Shkurina, T. N., Shostakovskiy, M. F., Sidel'kovskaya, F. P., Zelenskaya, M. G.

TITLE: Spectroscopic Investigation of N-Vinyllactams and Anilides

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk 1959, Nr 12, pp 2208-2212 (USSR)

ABSTRACT: Spectra of N-vinyllactams and anilides were studied, and the mutual influence of groups was investigated. Vinyllactams contain the system C=C—N—C=O; the examination of the interaction of atoms and groups can be simplified, to the first approximation, by considering the effect of the N-atom on C=C and C=O bonds, as well as the mutual interaction of the double bonds. Raman and UV-spectra of vinylpyrrolidone, vinylpiperidone, vinylcaprolactam, of various anilides (formanilide, acetanilide, etc.), and of simpler molecules containing an N-atom and a carbonyl group (pyrrolidone, N-butylpyrrolidone, caprolactam, dimethylacetamide were taken. Spectrograph

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