Spectroscopic Investigation of N-Vinyllactams and Anilides

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

ISP-51 and PRK mercury lamp were used to obtain Raman spectra, and spectrograph SF-4 to obtain UV-spectra. Spectra of vinyllactams in the double bonds region showed lines characteristic for $C=C$ and $C=O$ bonds. It was found that the presence of the N-atom at the double bond influenced considerably the spectral characteristics: the frequency of the $C=O$ bond was lowered nearly as much as in molecules containing $>N-C=O$ bonds. Values of the extinction coefficient of $C=O$ bond line in vinylpiperidone and vinylcaprolactam were quite high, and close to those of vinylamine. The intensity of $C=C$ line of vinylpyrrolidone was substantially higher, and that of $C=O$ line in all three vinyllactams was many times higher than in compounds with $>N-C=O$ bonds. This anomaly in the intensity of the $C=O$ bond in Raman spectrum was the most peculiar characteristic of vinyllactams which distinguished them from molecules with $C=C-N<$ and $>N-C=O$ bonds. It can be explained by the influence of the $C=C$ bond, through the N-atom, on the carbonyl group (in the bond system $C=C-N-C=O$). Similar

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Spectroscopic Investigation of N-Vinyllactams and Anilides

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relationships were also observed in anilide spectra. It was noted that the alkylation of N in anilides weakened the indications of conjugation of N with the benzene ring, and strengthened those of conjugation with the carbonyl group. It can be assumed, therefore, that a $C_6H_5NRCO \cdot X$ molecule loses the coplanarity of the system C_6H_5-N-C and the system C—N—COX becomes more planar. There are 3 tables; 1 figure; and 6 references, 1 U.S., 1 U.K., 1 German, 3 Soviet. The U.S. and U.K. references are R. Bowden, E. Braude, E. Jones, J. Chem. Soc., 1946, 948; E. Corey, J. Amer. Chem. Soc., 75, 2301 (1953).

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

SUBMITTED: April 7, 1958

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5.3620

77089
SOV/62-59-12-33/43

AUTHORS: Shostakovskiy, M. E., Prilezhayeva, Ye. N., Tsymbal, L. V., Azovskaya, V. A., Starova, N. G.

TITLE: Brief Communication. Concerning Addition of Nucleophilic Reagents to α, β -Unsaturated Sulfones in Presence of "Triton B"

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 12, pp 2239-2241 (USSR)

ABSTRACT: Addition of nucleophilic reagents (alcohols, mercaptans, hydrogen sulfide, dialkyldithiophosphoric acids, etc.) to α, β -unsaturated sulfones of various structures is catalyzed to a great extent by "Triton B" (benzyltrimethylammonium hydroxide). The addition reaction starts upon addition of a few drops of "Triton B" (40-60% aqueous solution, 0.2-0.5% by weight) to an equimolar mixture of reacting substances. In most cases the reaction is exothermic (temperature rises up to 80-100°) and is completed within 2-3 hr, with a nearly quantitative yield. α, β -Unsaturated sulfones,

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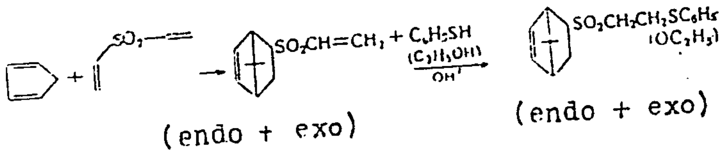
Brief Communication. Concerning Addition of Nucleophilic Reagents to α, β-Unsaturated Sulfones in Presence of "Triton B"

having other unsaturated bonds in the molecule (e.g., endo- and exovinyl bicycloheptenyl sulfones, obtained by reaction of cyclopentadiene with divinyl sulfone), add alcohol or mercaptan under these conditions only at the unsaturated bond activated by sulfone group:



Disulfones, having two unsaturated bonds, add two mercaptan molecules. Table 1 lists the yields and physical constants of the addition products (eight of them prepared to the first time) obtained by the authors.

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Brief Communication. Concerning Addition of Nucleophilic Reagents to α, β - Unsaturated Sulfones in Presence of "Triton B"

TABLE 1

FORMULA	YIELD IN %	bp IN °C (PRESSURE IN mm)	mp (°C)	FOUND %			CALC %.		
				C	H	S	C	H	S
$C_2H_5SO_2C_2H_4SC_2H_5$ **)	85,4	147—148,5 (3)	35—36	39,82	7,75	34,93	39,53	7,74	35,17
$C_2H_5SO_2C_2H_4SC_3H_7$ *)	99	—	32—33	42,93	8,22	32,42	42,82	8,21	32,66
$C_2H_5SO_2C_2H_4SC_4H_9$ *)	98	—	40—41	45,44	8,62	30,57	45,68	8,62	30,48
$C_2H_5SO_2C_2H_4SCH_2C_6H_5$ *)	90	—	56	54,04	6,64	26,10	54,06	6,60	26,24
$C_2H_5SO_2C_2H_4SC_6H_5$ ***)	90	124—125 (0,04)	39—40	52,05	6,03	27,68	52,14	6,12	27,90
$C_2H_5SO_2C_2H_4OH$	90	—	42—43	34,78	7,46	22,94	34,76	7,49	23,20
$C_2H_5SO_2C_2H_4OC_2H_5$ *)	91	125—130 (4)	—	43,40	8,42	19,30	43,39	8,49	19,29
$C_2H_5SO_2C_2H_4OC_4H_9$ -n) *)	89,6	116—116,5 (0,5)	—	49,37	9,37	16,44	49,45	9,34	16,50
$C_2H_5SO_2C_2H_4OCH_2CH_2OH$ *)	Сумм. 85,4	114—116 (0,03)	—	33,13	7,77	17,66	39,54	7,74	17,60
$(C_2H_5SO_2C_2H_4OCH_2)_2$ *)		188—190 (0,03)	—	39,55	7,33	21,19	39,71	7,33	21,21
$(C_2H_5SO_2C_2H_4)_2S$ *)	85	—	108—109	35,40	6,79	34,82	35,01	6,61	35,05
$C_2H_5SO_2C_2H_4SP(S)(OC_2H_5)_2$ ****)	34—43	133—137 (0,04)	—	31,46	6,18	31,43	31,35	6,25	31,40

(CONT.)

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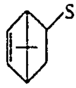
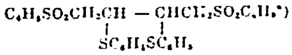
TABLE 1 (cont.)

77089, SOV/62-59-12-33/43

FORMULA	YIELD %	bp in °C (PRESSURE IN mm)	mp (°C)	FOUND %			CALC %		
				C	H	S	C	H	S
 $SO_2C_2H_4OC_2H_5$ *) (эндо + экзо)	Сумм. 94	85—85,5 (0,03)	—	56,95	8,06	13,93	57,36	7,88	13,92
		95—97 (0,03)	—	57,53	8,01	14,04			
 $SO_2C_2H_4SC_6H_5$ *) (эндо + экзо)	Сумм. 86	—	33	—	—	21,50	61,06	6,13	21,74
		—	47	61,32	6,27	21,70			
 $C_6H_5SO_2CH_2\underset{SC_6H_5}{CH}-\underset{SC_6H_5}{CH}CH_2SO_2C_6H_5$ *)	84	—	112—113	56,53	6,66	24,81	55,99	6,66	24,92

Notes: * Obtained for the first time. ** In the literature [Lorenz, W., Pat. FRG (Federal Republic of Germany), 876691 (5/18/1953); Referat. Zhur. Khim., Nr 32864 (1955)], it is described as a compound, liquid at room temperature, bp 127-129° (2 mm). *** Literature [Moore, A. H. Ford, J. Chem. Soc., 1949, 2433], mp 36-38°. **** Found: P 9.62; 10.00%. Calculated: P. 10.11%. In the literature [Thompson, R. B., Cheniceck, J. A., Symon, T., J. Ind. Eng. Chem., 50, 797 (1958)] it is described as "nonvolatile residue".

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Brief Communication. Concerning Addition of Nucleophilic Reagents to α,β-Unsaturated Sulfones in Presence of "Triton B"

77089
SOV/62-59-12-33/43

There is 1 table; and 6 references, 2 Soviet, 1 German, 1 U.K., 2 U.S. The U.K. and U.S. references are: A. H. Ford, Moore, J. Chem. Soc. 1949, 2433; J. L. Szabo, E. T. Stiller, J. Amer. Chem. Soc. 70, 3667 (1948); Ch. D. Hurd, L. L. Gershbein, J. Amer. Chem. Soc. 69, 2328 (1947); R. B. Thompson, J. A. Cheniceck, T. Symon, J. Industr. and Engng. Chem., 50, 797 (1958).

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SUBMITTED: May 4, 1959

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

Tin organic polymers. Vysokom. soed. 1 no.3:482-484 Mr '59.
(MIRA 12:10)

1.Nauchno-issledovatel'skiy institut promyshlennosti plasticheskikh mass.
(Polymers) (Tin organic compounds)

SHOSTAKOVSKIY, M.F.; PRILEZHAYEVA, Ye.N.; KARAVAYEVA, V.M.

Synthesis of sulfur compounds from vinyl ethers and acetylene. Part 19: Role of thionic complexes in the ionic polymerization of sulfur-containing vinyl compounds. Vysokom.soed. 1 no.4:582-582-589 Ap '59. (MIRA 12:9)

1. Institut organicheskoy khimii AN SSSR im. N.D.Zelinskogo.
(Polymerization) (Vinyl compounds)

SHOSTAKOVSKIY, M.F.; PRILEZHAYEVA, Ye.N.; KARAVAYEVA, V.M.

Synthesis of sulfur compounds from vinyl ethers and acetylene. Part 20: Interaction of mercaptals with vinyl sulfides and vinyl ethers. Vysokom.soed. 1 no.4:590-593 Ap '59. (MIRA 12:9)

1. Institut organicheskoy khimii AN SSSR im. N.D.Zelinskogo.
(Sulfur compounds) (Vinyl compounds)

SHOSTAKOVSKIY, M.F.; PRILEZHAYEVA, Ye.N.; KARAVAYEVA, V.M.

Synthesis of sulfur compounds from vinyl ethers and acetylene. Part 21: Ionic copolymerization of vinyl sulfides with styrene and vinylbutyl ether. Vysokom soed. 1 no.4:594-596 Ap '59. (MIRA 12:9)

1. Institut organicheskoy khimii AN SSSR im. N.D.Zelinskogo.
(Polymerization) (Sulfur compounds)

SHOSTAKOVSKIY, M.F.; PRILEZHAYEVA, Ye.N.; KARAVAYEVA, V.M.

Determination of relative activity coefficients in copolymerization of vinylethlsulfide with styrene and methylmethacrylate. Vysokom.soed. 1 no.5:781-783 My '59. (MIRA 12:10)

1. Institut organicheskoy khimii im. N.D.Zelinskogo.
(Sulfide) (Styrene) (Methacrylic acid)

67037

5.3831
~~5 (1), 5 (3)~~

SOV/153-2-5-22/31

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

TITLE: Synthesis and Polymerization of Vinyl Sulfides

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1959, Vol 2, Nr 5, pp 761 - 768 (USSR)

ABSTRACT: At the Laboratory for Vinyl Compounds of the Institute in which the authors work, the synthesis methods and the chemical changes of vinyl compounds, which contain, besides double bonds such hetero atoms as O,S,N,Si, etc, have been studied for several years. The present paper gives a review on the studies of the synthesis of monomers of this group containing sulfur, some of their reactions, the polymerization and the copolymerization. A general method of synthesis was developed (Ref 5) based on a modification of the vinylization reaction according to A. Ye. Favorskiy and M. F. Shostakovskiy (1) (Ref 6). An excess of acetyls still remains to be a necessary condition. The vinylization of mercaptanes yields several advantages (Refs 7,9,10). From alkyl-mercaptanes and di-acetyls (Refs 11,12) it is possible to obtain the corresponding alkyl-thio-butenine (Equation (3), Table 1) at 30-50°C, in a methanol medium and in the presence of

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SOV/153-2-5-22/31

Synthesis and Polymerization of Vinyl Sulfides

2-3% of KOH. The authors developed, instead of the acid hydrolysis to the acetaldehyde and a titration of the latter, the splitting of the vinyl sulfides by an alcoholic sublimate solution as a method for quantitative determination (Refs 7,8) (4). This reaction (4) is also suited for alkyl-thio-butenines (Refs 11,12). The authors also established the conditions of the selective sulfur oxidation in vinyl-alkyl sulfides in which vinyl sulfoxides or vinyl sulfones form (Table 2). These can be used as starting substances for polymerization (5). The introduction of the sulfur increases the dielectric properties of the polymer (Ref 19) and its thermoplasticity (Ref 16). By introducing the sulfone groups, the benzo-resistance increases (Ref 20). It was observed that vinyl sulfides have less inclination to kationic polymerization under the influence of metal halides, but they easily form polymers under the influence of a suitable free-radical initiator. The best yield of ionic polymers was obtained in the presence of tri-boron-fluoride-ethyrate (Ref 21). The polymers are viscous oils. For the determination of their molecular weight, titration of the thio-vinyl terminal groups by sublimate was used besides cryoscopy (see also above). Good accordance confirms the structure of the terminal groups

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Synthesis and Polymerization of Vinyl Sulfides SOV/153-2-5-22/31

to be $-CH=CHSR$. Table 3 shows the fractionation of a sample of polyvinyl-ethyl sulfide. Tables 4 and 5 illustrate the conditions of polymerization of vinyl sulfides in the presence of free-radical initiators and the properties of the polymers obtained. The best yields were obtained with dinitrile of the azo-isobutyric acid. Benzoyl-peroxide cannot be used in this case (Ref 23). No thione groups form on introduction of a free radical and the terminal groups of the polymers have also the character of a thio-vinyl (7). 12 pairs of monomers containing vinyl sulfides were studied on copolymerization. The properties of the copolymers are also studied. Table 6 shows the polymerization of the vinyl-ethyl sulfone. The rules established can be explained in view of the reciprocal influence of the $C=C$ linkage and the sulfur atom in the vinyl-sulfide molecule. There are 6 tables and 31 references, 24 of which are Soviet.

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

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67038

5.3831

~~5 (1), 5 (3)~~ SOV/153-2-5-23/31

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

TITLE: Synthesis of New Monomers on the Basis of Acetylene and Diacetylene

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1959, Vol 2, Nr 5, pp 769 - 775 (USSR)

ABSTRACT: From acetylene and diacetylene, as well as from compounds containing a mobile hydrogen, monomers (ether and thioether) with a vinyl-ethyl-vinyl- and a diene group can be obtained. The compounds with mobile hydrogen are in particular: alcohols of various structure, amino alcohols, mercaptanes, phenols, silanols, etc. According to the method of A. Ye. Favorskiy and M. F. Shostakovskiy different types of vinyl compounds with a total formula $CH_2{=}CH{-}XR$ can be obtained where X = O,N,S,Si, and R is an alkyl, aromatic, hydroaromatic, or other radical (Ref 1). The most interesting among the recently obtained unsaturated compounds on acetylene basis, is the vinyl-ether of the amino alcohols (Refs 5,6). They may be used as initial raw materials for several nitrogen-containing macromolecular products including some with

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Synthesis of New Monomers on the Basis of Acetylene and Diacetylene

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SOV/153-2-5-23/31

a three-dimensional structure (to be used as ion-exchanger resins). At present diacetylene becomes interesting because it may serve as a starting raw material for various syntheses, and because it has both a scientific and a practical significance. In the laboratory for vinyl compounds of the Institute in which the authors work, the hitherto neglected chemistry of the diacetylenes concerning the interaction with compounds containing mobile hydrogen has been systematically studied. By the reaction of diacetylene with alcohols (Ref 8) and mercaptanes (Ref 10) (constants of the reaction products in Table 1), as well as with amino alcohols (Ref 10) organic compounds with a simple ether (also containing nitrogen) and with a thio-ether-group in the conjugated system of the double and triple linkages (I) can be obtained. Additionally, butadiene-α-ether (II), α,δ-di-thio-ether (III) and mixed α,δ-thio-ether are obtained. The synthesis method of the 1-alkoxy-butadienes-1,3 on the diacetylene and the alcohol basis makes possible the production of several representatives of this class which contain alkyl- and cyclic radicals (Ref 16). The alcohols react with diacetylene under the influence of alkali and on heating. In this reaction, ethyl-vinyl-

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Synthesis of New Monomers on the Basis of Acetylene and Diacetylene SOV/153-2-5-23/31

ether (I) and acetals of butin-2-al-4(see Scheme) are formed. The reaction of the diacetylene with mercaptanes occurs gradually. Unlike the reaction with alcohols, the 2-mercaptane molecule adds itself to the threefold linkage and di-thio-alkyl (or phenyl) of the butadiene-1,3 is formed (Scheme). The compounds produced are highly reactive. The authors recommended a new method of synthesis for the 1-alkoxy-butadiene-1,3 based on partial hydration of the ethyl-vinyl-ether (Table 4). Tables 2,3,5, and 6 list the constants of additional products synthesized. Finally, they established the conditions of the synthesis of vinyl ether of ethanol amines of various structures, and examined their properties. There are 6 tables and 18 references, 13 of which are Soviet.

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

Card 3/3

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

Investigations in the field of the synthesis and transformation of unsaturated silicon organic compounds. Dokl.AN Azerb.SSR 15 no.1:21-23 '59. (MIRA 12:3)

1. Institut organicheskoy khimii AN SSSR i Institut nefti AN AzerSSR. Predstavleno akademikom AN AzerSSR Yu.G.Mamedaliyevym.
(Silicon organic compounds)

27214

S/081/61/000/014/011/030
B103/B217

5.3700

AUTHORS: Shostakovskiy, M. F., Vlasov, V. M.

TITLE: Synthesis of some trialkyl silanols

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 14, 1961, 257, abstract 14Ж289 (Sb. nauchn. rabot Yaroslavsk. med. in-ta, 1959, vyp. 22, 511-514)

TEXT: Pure $R_2R'SiOH$ (Ia-b; here and in the following a) $R = CH_3$, $R' = C_2H_5$; b) $R = C_2H_5$, $R' = CH_3$) suited for optical studies were synthesized as follows: $R_2R'SiCl$ (II) + ethylene oxide (III) $\longrightarrow R_2R'SiOCH_2\ CH_2Cl$ (IV) $\xrightarrow{2}$ I + $HOCH_2CH_2OH$ (V). A weak stream of III is conducted through the ethereal solution of 0.1 mole of IIa up to the required overweight (20 - 25°C) and (here and in the following, the yield is given in %, and the boiling point in °C/mm, $n^{20}D$, d_4^{20}) 93, 71-72/39, 1.4316, 1.4260, 0.9469 of IVa are isolated. Similarly 91.8, 67-68/13,

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S/081/61/000/014/011/030
B103/B217

Synthesis of some trialkyl silanols

0.9478 of IVb were obtained from 0.1 mole of IIb and III. 5 % NaOH and 3-4 drops of phenol phthalein are added to the ethereal solution of 18 g of IVb, and the mixture is vigorously stirred for 1 hr. 72, 61-62/30, 1.4204, 0.8456 of Ib are isolated from the ethereal layer by the usual treatment after 3 hr when the color of the indicator has vanished). V was separated from the aqueous layer in a yield of 66.1 %. 86, 58/50, 1.4070, 0.8335 of Ia were obtained from 0.1 mole of IVa under similar conditions. [Abstracter's note: Complete translation.]

X

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5 (3) SOV/74-28-6-4/5

AUTHORS: Shostakovskiy, M. F., Komarov, N. V.
Shikhiyev, I. A.

TITLE: Silanols (Silanoly)

PERIODICAL: Uspekhi khimii, 1959, Vol 28, Nr 6, pp 741 - 771 (USSR)

ABSTRACT: The present paper describes the methods of synthesis and the properties of silanols. Silanols are compounds containing hydroxyl groups directly bound to the silicon atom. Owing to particular affinity of the silicon atom to oxygen, there are silicon-organic compounds with one, two and three hydroxyl groups with the silicon atom. In this connection, they are classified into alkyl (aryl) silanols with the common formula R_3SiOH, silandiols $R_2Si(OH)_2$, and silantriols $RSi(OH)_3$. Of the mentioned compounds, the trialkyl (aryl) silanols are best investigated. They are highly reactive compounds and have great practical and theoretical importance. In contrast to silicon-organic alcohols, there are a number of common methods of synthesis for silanols. For some representatives of this class, there are quite special methods of synthesis peculiar to them. Of the methods of synthesis, the following were described:

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SOV/74-28-6-4/5

Silanols

the hydrolysis of halogen silanes (Refs 8, 10-63), of alcoxysilanes (Refs 25,35,64-75), of acetoxysilanes (Refs 10,76-81), of aminosilanes (Refs 10,21,82-90), the magnesium-organic synthesis (Refs 91-95), the cleavage of siloxanes (Refs 95-103), the cleavage of tetrasubstituted silanes (Refs 102,104-124), and the hydrolysis of hydride silanes (Refs 35,60,84,128-132). Besides the mentioned general methods of obtaining silanols, special publications describe many other methods which are suitable for the synthesis of compounds with a certain structure (Refs 5,24,31,102,103,111,124,133-147). The physical properties of many silanols have not yet been fully characterized (Table). For some representatives, the physical constants are contradictory. In spite of this, certain rules referring to their physico-chemical properties can be determined from the data indicated in the table of the compounds of this class (Refs 32,148-155). Trialkyl (aryl) silanols remind of tertiary alcohols as to their structure. Silandiols and silantriols have no analoga among organic compounds. Silanols are, in general, similar to the corresponding organic alcohols, but by the presence of the silicon atom their properties attain a character peculiar to them. This brings about that in many ca-

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SOV/74-28-6-4/5

Silanols

ses they react differently from alcohols. Some of these reactions were considered closely and compared with the corresponding reactions of organic analoga: action of metals and lyes (Refs 8,12,31,43,60,68,81,96-103,203,205-222), dehydration of silanols (Refs 4,24,26,33,35,37,46,47,60,63,68,190,224-226), interaction with halogen silanes (Refs 11,21,128,227,230,231), action of mineral acids (Refs 31,62,228,232,233), interaction with acid anhydrides and halogen anhydrides (Refs 22,31,41,61, 223,227,324,235), interaction with alcoxysilanes (Refs 21,230, 236-239), reaction with vinyl ether (Refs 52,80,87-90,226,240-244), action of Fischer's reagent (Refs 169,245), interaction with isocyanates (Refs 37,51,183,246), hydration of silanols (Refs 37,247). As mentioned before, silanols are highly reactive substances which are capable of undergoing various reactions. Some of these reactions were described (Refs 37,21,49,53, 81,102,139,167,169,172,206-209,223,249-264).Silanols are used in industry for the production of various resins (Refs 257-265), heat-resisting coats (Refs 203,209), bactericide substances (Ref 265), adhesives (Refs 267,268), water-repellent agents (Refs 210,268), for impregnating paper (Ref 270), as diffusion

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Silanols

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liquids (Ref 237), for lubricating oils (Ref 237) and for many other substances. There are 1 table and 270 references, 65 of which are Soviet.

ASSOCIATION: In-t organicheskoy khimii im. N. D. Zelinskogo AN SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, AS USSR)

Card 4/4

5 (3)

AUTHORS: Shostakovskiy, [redacted] Bogdanova, A. V., SOV/74-28-9-3/7
Krasil'nikova, G. K.

TITLE: Diacetylene and Its Derivatives

PERIODICAL: Uspekhi khimii, 1959, Vol 28, Nr 9, pp 1052-1085 (USSR)

ABSTRACT: In the present paper the authors give a survey on the actual state of the chemistry of acetylene and its derivatives. First, the methods of obtaining these substances are described: the synthesis of the diacetylene derivatives from acetylene and other substituents among them dimerisation of mono-substituents, acetylenes (Refs 1-27); magnesium-organic synthesis (Refs 28-31); dehalogenation of halogen derivatives (Refs 32-37). The methods for obtaining diacetylene can be subdivided into three groups: The syntheses of the first group based on the oxidative dimerisation of metallic salts of the acetylene have, at present, only a historical value (Refs 34, 38-41). The second group comprises methods using the effect of an electric discharge on various hydrocarbons (Refs 42-48). The third group comprises the syntheses based on a gradual splitting-off of elements of the halogen hydracids from the halogen derivatives of the butane series (Refs 49-71). The

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SOV/74-28-9-3/7

Diacetylene and Its Derivatives

physical properties of diacetylene are treated according to references 31, 32, 39, 40, 45, 75-90, and its explosive properties according to references 39, 42, 47, 91-95. The purification and the analytical determination of acetylene are described according to the references 45, 48, 57, 59, 60, 72, 97-100. Then follows the description of the chemical properties of diacetylene and its derivatives. Diacetylene is the first member of the homologous polyine series with conjugated triple bonds. The separation of first acetylene compounds from vegetable products stems from the year 1892 (Ref 101). Since that time about 50 of such compounds have been obtained. References 17, 18, 102-107 are devoted to a close investigation of the separation and of the synthesis. The informations contained in publications on the properties of diacetylene and its derivatives chiefly refer to the reactions of substitution and addition. Among the substitutions we find the reactions with magnesium-organic compounds (Refs 29, 31-34, 49, 55, 98, 108-115); with metals (Refs 51, 54, 57, 100, 111, 116); with halogens (Ref 31) with carbonyl compounds (Refs 7, 10, 46, 48, 117-122), and with methyl olamines. The field of additions

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to diacetylene covers: the addition of hydrogen (Refs 123-127, 29, 32, 55), of halogens (Refs 29-32, 128-132); of nitrogen dioxide (Refs 133-135); of water (Refs 66, 99, 136); of alcohols (Refs 48, 57-59, 62, 65-67, 137-140), of glycols (Ref 137); of mercaptans (Refs 62, 141), of amino alcohols (Refs 48, 63, 122); of acrylonitrile (Refs 142-144); of HCN (Ref 145), of thiocyanogen (Ref 146) and of dialkylamines (Ref 48). Furthermore, the oxidative dimerisation of the diacetylenes is described (Refs 1, 4, 6, 7, 17, 18, 29, 33, 101, 105-107, 147, 148). The following section of the paper is devoted to the ethinyl compounds. The physical properties and the spectra of the ethinyl vinyl ester are described, as ascertained by the authors. Among the chemical reactions of the ethinyl vinyl ester the substitutions of acetylene hydrogen and the addition are the most investigated. Substitutions were investigated in reactions with metal (Refs 57, 11), with ketones (Ref 149), and with the magnesium-organic compounds (Refs 150-151). Additions to ethinyl vinyl ester were investigated in reactions with alcohols (Refs 58, 59, 62, 65, 66, 91, 137, 138, 150-153) with mercaptans (Refs 62, 156-158); with water (Refs 57-60, 64, 159); with carbonyl-compounds (Refs 48, 57, 124, 150, 160-162); with

Diacetylene and Its Derivatives SOV/74-28-9-3/7

acetals of acetaldehyde (Refs 163, 164); with bromine (Ref 59). Furthermore, the addition of hydrogen (Refs 59, 158, 165-173) and the dimerisation of ethinyl vinyl ester (Refs 17, 21, 148, 174) were investigated. Finally, ethinyl vinyl thioester (Refs 62, 156-158, 175); ethyl vinyl ester, containing N (Refs 63, 67) and ethinyl vinyl ester, containing Si were produced. The table contains a list of some of the functional diacetylene derivatives. The following Soviet authors are mentioned: V. I. Yegorova, O. M. Kuznetsova, G. I. Plotnikov, I. A. Chekulayeva, L. V. Kondrat'yev, I. I. Strizhevskiy, M. D. Ohekhovich, Zh. I. Iotsich, E. S. Shapiro, and L. I. Shmonina. There are 1 table and 176 references, 33 of which are Soviet.

ASSOCIATION: In-t organicheskoy khimii AN SSSR, im. N. D. Zelinskogo (Institute of Organic Chemistry AS USSR imeni N. D. Zelinskiy)

Card 4/4

Synthesis and Transformations of Organosilicon Vinyl Ethers

SOV/79-29-2-5/71

The affiliation of alcohols, silanols, and organic acids to the γ-silicon-containing vinyl ethers takes place under the influence of acid catalysts according to the ion mechanism, in agreement with Markovnikov's rule. On their reaction with organosilicon alcohols and silanols, hitherto unknown acetals were obtained, containing silicon atoms in both alcohol radicals. The reaction of these ethers with organic acids can serve as a basis for the synthesis of a new class of organosilicon compounds, i.e. organosilicon acylates. Hydrogenation, chlorination, and hydrochlorination of the γ-silicon-containing vinyl ethers were investigated. There are 3 tables and 12 Soviet references.

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

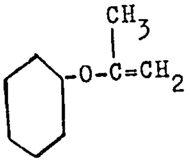
SUBMITTED: November 5, 1957

Card 2/2

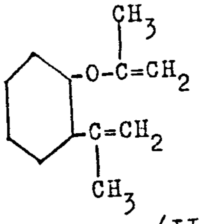
SOV/79-29-5-30/75

Investigation in the Field of the Synthesis and Transformation of Substituted Vinyl Ethers. 9. Formation and Nature of Resin-like Products Obtained in the Vinylation of Phenols

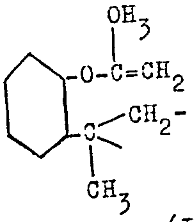
on the ratio methyl acetylene : phenol. The yield in resin increases with rising methyl acetylene content. The investigation of the distilled resin fractions by the aid of chemical and spectroscopic methods has shown that they are mixtures of the products (I - III).



(I)



(II)



(III)

The fraction boiling at 110-115° (3mm) represents the o-isopropenyl-isopropenylphenyl ether (II). This was confirmed by elementary analysis, hydrolysis, by the determination of the molecular fraction and by spectral analysis. Fractions that

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SOV/79-29-5-30/75

Investigation in the Field of the Synthesis and Transformation of Substituted Vinyl Ethers. 9. Formation and Nature of Resin-like Products Obtained in the Vinylation of Phenols

are distilled at higher temperatures are mixtures of the polymer (III) of different polymerization degrees with the monomer. Ultraviolet and infrared spectra were taken at the opticheskaya laboratoriya IOKh AN SSSR (Optical Laboratory IOKh AS USSR) by B. V. Lopatin. There are 13 references, 3 of which are Soviet.

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

SUBMITTED: March 12, 1958

Card 3/3

5 (3)

SOV/79-29-5-31/75

AUTHORS: Shikhiyev, I. A., Shostakovskiy, M. F., Komarov, N. V. Aslanov, I. A.

TITLE: Investigations in the Field of Synthesis and Transformations of Unsaturated Organo-germanium Compounds (Issledovaniya v oblasti sinteza i prevrashcheniy nepredel'nykh germaniyorganicheskikh soyedineniy). I. Synthesis of Mono-, Di-, and Trisubstituted Tertiary γ-Germanium Acetylene Alcohols (Sintez odno-, dvukh- i trekhatomnykh tretichnykh γ-germaniyatsetilenovykh spirtov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1549-1551 (USSR)

ABSTRACT: In a previous paper (Ref 1) the reaction of di-magnesium-dibromodimethyl-ethinyl carbinol (Iotsich Reagent) with various alkyl-(aryl)-chlorosilanes was investigated. In order to explain further the reaction process with this reagent, its influence upon methyl-, dimethyl-, and trimethyl germanium bromides was investigated. The reaction was found to proceed with the formation of tertiary γ-germanium containing acetylene alcohols according to the following scheme:

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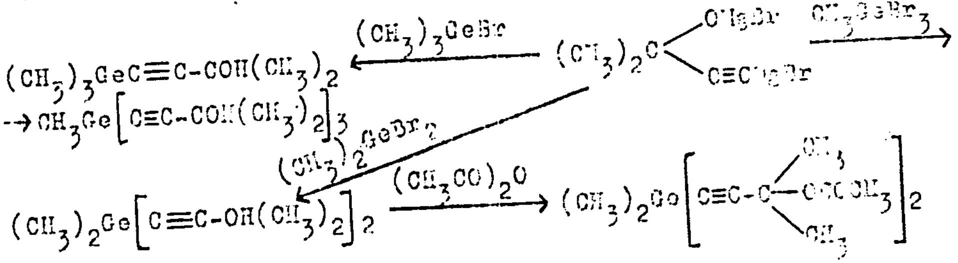
SOV/79-29-5-31/75

Investigations in the Field of Synthesis and Transformations of Unsaturated Organo-germanium Compounds. I. Synthesis of Mono-, Di-, and Trisubstituted Tertiary γ-Germanium Acetylene Alcohols



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

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SOV/79-29-3-31/75

Investigations in the Field of Synthesis and
Transformations of Unsaturated Organo-germanium Compounds. I. Synthesis of
Mono-, Di-, and Trisubstituted Tertiary γ-Germanium Acetylene Alcohols

germanium. There are 3 Soviet references.

SUBMITTED: November 25, 1957

Card 3/3

SOV/79-29-7-7/83

5(3)

AUTHORS: Shikhiyev, I. A., Shostakovskiy, M. F., Kayutenko, L. A.

TITLE: Investigations in the Field of the Synthesis and the Transformations of Unsaturated Organo-silicon Compounds (Issledovaniya v oblasti sinteza i prevrashcheniy nepredel'nykh kremneorganicheskikh soyedineniy).
II. Synthesis of the Silicon Hydrocarbons of the Vinyl Acetylene Series (II. Sintez kremneuglevodorodov vinilatsetilenovogo ryada)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2137-2139 (USSR)

ABSTRACT: The synthesis of acetylene alcohols (Ref 1), their hydrogenation and dehydration (Refs 2, 3) as well as the affiliation of various compounds to the triple bond (Refs 1, 4, 5) is of high theoretical and practical interest. Similar conversions of the organo-silicon acetylene alcohols were carried out for a comparative investigation of their properties. Earlier, the authors elaborated the synthesis of mono- (Ref 6), bi- (Ref 7), and trivalent (Ref 8) γ-silicon and γ-germanium substituted (Ref 9) acetylene alcohols. In the present paper the dehydration conditions of some γ-silicon substituted ditertiary acetylene glycols as well as the catalytic hydrogenation of the

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Investigations in the Field of the Synthesis and the Transformations of Unsaturated Organo-silicon Compounds. II. Synthesis of the Silicon Hydrocarbons of the Vinyl Acetylene Series

silicon hydrocarbons obtained were investigated according to the afore mentioned scheme. Thus, the synthesis of vinyl acetylene silicon hydrocarbons was elaborated by the dehydration of the corresponding ditertiary γ-silicon substituted acetylene glycols in the presence of $KHSO_4$. The following compounds were obtained and characterized: bis-(2-methyl-butene-1-in-3)-ethyl silane; bis-(2-methyl butene-1-in-3)-diethyl silane; bis-(2-methyl butene-1-in-3)-dimethyl silane; bis-(2-methyl butene-1-in-3)-methylethyl silane, and bis-(2-methyl butene-1-in-3)-methyl propyl silane. By catalytic hydrogenation of bis-(2-methyl butene-1-in-3)-diethyl silane the corresponding saturated silicon hydrocarbon, diethyl diisoamyl silane, was

Investigations in the Field of the Synthesis and the SOV/79-29-7-7/83
Transformations of Unsaturated Organo-silicon Compounds. II. Synthesis of the Silicon Hydrocarbons of the Vinyl Acetylene Series

synthesized. The silicon hydrocarbons synthesized are more exactly characterized in the table. There are 2 tables and 9 references, 8 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR i Institut neftekhimicheskikh protsessov Akademii nauk Azerbaydzhanskoy SSR (Institute of Organic Chemistry of the Academy of Sciences USSR and Institute of Petrochemical Processes of the Academy of Sciences of the Azerbaydzhanskaya SSR)

SUBMITTED: July 3, 1958

Card 3/3

SHOSTAKOVSKIY, M.F., doktor khim.nauk

Large chemicals industry of Irkutsk Province. Znan.sila 34 no.3:22-23 Mr '59. (MIRA 12:4)

1. Direktor Irkutskogo instituta organicheskoy khimii.
(Irkutsk Province--Chemicals industry)

5(3)

AUTHORS: Shostakovskiy, M. F., Bogdanova, A. V., Plotnikova, G. I. SOV/20-124-1-30/69

TITLE: Investigation in the Field of Diacetylene Derivatives (Issledovaniye v oblasti proizvodnykh diatsetilena) Interaction Between Diacetylene and Phenols, Thiophenol and Benzyl Alcohol (Vzaimodeystviye diatsetilena s fenolami, tiofenolom i benzilovym spirtom)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 1, pp 107 - 110 (USSR)

ABSTRACT: The authors had earlier reported on syntheses based on diacetylene with aliphatic and hydro-aromatic alcohols as well as with ethyl mercaptan (Refs 1,2). In order to introduce the corresponding aryl derivatives into the substances available the authors tried to add phenol to the diacetylene. These two substances, however, did not react together according to the usual scheme under conditions suitable for alcohols. The authors wanted to investigate the reaction mentioned in the subtitle. They wanted to eliminate the influence of the benzene nucleus which is caused by the oxygen atom. This

Card 1/3

was expected to be changed by means of the sulfur atom in thiophenol and by the distance of the benzene nucleus from the oxygen. In fact, both reactions proceeded smoothly under gentle conditions (1). The junction of the second molecule of the benzyl alcohol or of thiophenol forms the next stage of the reaction and can also proceed independently. In the case of benzyl alcohol, this stage proceeds according to the ionic mechanism. Butinal-dibenzyl-acetal $CH_3-C \equiv C-CH(OCH_2C_6H_5)_2$ (III) is formed. In the case of thiophenol the second stage of the interaction with diacetylene proceeds mainly under the influence of radical initiators. Dithio derivatives of butadiene-1,3 are formed. Thus, either thiophenol or ethyl mercaptan is added to ethyl vinyl thiophenyl ether yielding dithiophenyl- and thiophenyl-thioethyl-butadiene-1,3 (2), respectively. This reaction is accelerated by KOH, azo-isobutyric acid-nitrile or by increased temperature. The yield of the end products depends on the temperature and on the initiator. Dithiophenyl- and thiophenyl-thioethyl-butadiene-1,3 undergo the diene synthesis with maleic acid anhydride, forming adducts that

Investigation in the Field of Diacetylene Derivatives. SOV/20-124-1-30/69
Interaction Between Diacetylene and Phenols, Thiophenol and Benzyl Alcohol

lose two mercaptan molecules and forming phthalic anhydride (Refs 2,6). An experimental section (not designed as such) ensues. There are 3 tables and 6 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)

PRESENTED: May 17, 1958, by B. A. Kazanskiy, Academician

SUBMITTED: May 15, 1958

Card 3/3

SHOSTAKOVSKIY, M.F

SOV/4989

PHASE I BOOK EXPLOITATION

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

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

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

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

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

Card 1/7

coatings, silicon rubber, lubricants, and hydrophobic and gluing materials. The book also describes the new oxygen-containing organosilicon compounds such as organosilicon alcohols and silanols, simple vinyl ethers and their derivatives, and organosilicon acetals and acylals. The production and properties of chlorosilanes are described briefly. B. N. Dolgov, K. A. Andrianov, and A. P. Kreshkov are cited as Soviet writers on the chemistry of organosilicon compounds. References accompany each chapter.

TABLE OF CONTENTS:

SOV/4982

International symposium on macromolecular chemistry, Moscow, 1960.

Mezhdunarodnyy simpozium po makromolekulyarnoy khimii SSSR, Moskva, 14-18 iyunya 1960 g.; doklady i avtoreferaty. Sektsiya I. (International Symposium on Macromolecular Chemistry Held in Moscow, June 14-18, 1960; Papers and Summaries. Section I.) [Moscow, Izd-vo AN SSSR, 1960] 346 p. 5,500 copies printed.

Sponsoring Agency: The International Union of Pure and Applied Chemistry, Commission on Macromolecular Chemistry

Tech. Ed.: T. V. Polyakova.

PURPOSE: This collection of articles is intended for chemists and researchers interested in macromolecular chemistry.

COVERAGE: This is Section I of a multivolume work containing scientific papers on macromolecular chemistry in Moscow. The material includes data on the synthesis and properties of polymers, and on the processes of polymerization, copolymerization, polycondensation, and polyrecombination. Each text is presented in full or summarized in French, English, and Russian. There are 47 papers, 28 of which were presented by Soviet, Rumanian, Hungarian, and Czechoslovakian scientists. No personalities are mentioned. References accompany individual articles.

Card 6/9

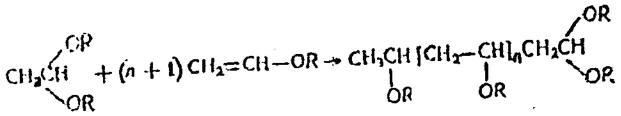
49

SHOSTAKOVSKIY, M. F.

78083
SOV/62-60-1-29/37

5.3400

AUTHORS:	Shostakovskiy, M. F., Gladyshevskiy, V. A., Baykova, R. I.
TITLE:	Brief Communications. Stepwise Synthesis of Poly(Vinyl Isopropyl Ether)
PERIODICAL:	Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, Nr 1, pp 138-139 (USSR)
ABSTRACT:	Stepwise polymerization of vinyl isopropyl ether was studied. The reaction proceeds as follows:



$$CH_3CH(OR)_2 + (n+1)CH_2{=}CH{-}OR \rightarrow CH_3CH(OR)[CH_2{-}CH(OR)]_nCH_2CH(OR)_2$$

where n = 0,1,2,3,etc. 1,1,3-Triisopropoxybutane (I) (25%), bp 77.5-78° (4 mm), d_4^{20} 0.8600, was obtained at

Card 1/2

Brief Communications. Stepwise Synthesis of Poly(Vinyl Isopropyl Ether)

78083
SOV/62-60-1-29/37

45° from diisopropyl acetal and vinyl isopropyl ether in the presence of 5% alcoholic $FeCl_3$. 1,1,3,5-Tetra-isopropoxyhexane (II) (15%), bp 115° (2 mm), n_D^{20} 1.4220, d_4^{20} 0.8787, was obtained under the same conditions as I, from I and vinyl isopropyl ether. 1,1,3,5,7-Pentaiso-propoxyoctane (III) (12%), bp 167-168° (1 mm), n_D^{20} 1.4300, d_4^{20} 0.8940, was also obtained under the same conditions as I, from II and vinyl isopropyl ether. The above polyethers were hydrolyzed with NaOH. The extent of hydrolysis was 98.7-99%. There are 1 table; and 4 Soviet references.

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

SUBMITTED: June 19, 1959

Card 2/[illegible]

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

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

(Favorskii, Aleksei Efgrafovich, 1860-1945)

SHOSTAKOVSKIY, M.F.

A.E. Favorskii's contributions to the development of the
chemistry of high molecular weight compounds (on the 100th
anniversary of A.E. Favorskii's birth). Izv.AN SSSR.Otd.khim.
nauk no.5:769-778 My '60. (MIRA 13:6)
(Favorskii, Aleksei Evgrafovich, 1860-1945)
(Macromolecular compounds)

S/062/60/000/006/020/025/XX
BC20/B060

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

TITLE: Acetylene-diene Isomerization of 1,4-Dichloro Butane-2 and Syntheses Performed on Its Basis. Communication 1. Action of Water-methanol- and Methanol Solutions of Potassium Hydroxide on 1,4-Dichloro Butyne-2

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 6, pp. 1098-1103

TEXT: The authors oxidized 1,4-dichloro butyne-2 with permanganate and obtained monochloroacetic acid as the only reaction product. Proceeding from the assumption that in the dehydrochlorination of 1,4-dichloro butyne-2 by means of an alcoholic KOH solution the separation of hydrogen chloride from one and the same carbon atom is improbable, the attempt was made to prove the course of an isomerization on the basis of the reaction products. From among the compounds produced by the reaction mentioned in the title, the following were identified and described: 2-chloro-buten-1-

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Acetylene-diene Isomerization of 1,4-Dichloro Butane-2 and Syntheses Performed on Its Basis. Communication 1. Action of Water-methanol- and Methanol Solutions of Potassium Hydroxide on 1,4-Dichloro Butyne-2

S/062/60/000/006/020/025/XX
B020/B060

methanol to 1,4-dichloro butyne-2 (I) in the presence of KOH at a temperature below 50°C was likewise observed. When an aqueous KOH solution is added to a methanol solution of (I) at about 65°C, diacetylene is obtained as the main product. The structure of the resulting 2-chlorobuten-1-ine-3 was confirmed by the spectroscopic analysis made by Lopatin. A description is given of the methods applied to confirm the structure of the remaining isolated compounds. Production, characteristic reactions, and identification of compounds (I) to (VIII) are also discussed. On the strength of results obtained, a mechanism of acetylene-allene-diene isomerization of 1,4-dichloro butyne-2 in water-methanol- and methanol KOH solution is suggested. V. R. Skvarchenko (Ref. 7), Yu. S. Zalkind, and M. L. Ayzikovich (Ref. 9), as well as V. I. Yegorova and O. M. Kuznetsova (Ref. 10) are mentioned. There are 13 references: 8 Soviet, 4 German, and 1 British.

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Acetylene-diene Isomerization of 1,4-Dichloro Butane-2 and Syntheses Performed on Its Basis. Communication 1. Action of Water-methanol- and Methanol Solutions of Potassium Hydroxide on 1,4-Dichloro Butyne-2

S/062/60/000/006/020/025/XX
B020/B060

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

SUBMITTED: November 18, 1958

Card 4/4

81935

Studies in the Field of Chemical Transformations of Unsaturated and High-molecular Compounds. 14. Copolymerization of Trivinylglycerol Ether With Methacrylic Acid and Its Methyl Ester

S/062/60/000/06/06/011
B020/B061

methacrylic acid and its methyl ester were used. On the examination of the conditions of copolymerization of trivinylglycerol ether with methacrylic acid, the following reactions may be expected: a) formation of copolymers containing free vinyl groups, b) formation of branched copolymers, and c) formation of three-dimensional copolymers insoluble in organic solvents. From this it follows that the copolymerization of trivinylglycerol ether and methacrylic acid takes place in several directions, and a complicated mixture of copolymers is formed. No formation of three-dimensional copolymers was found on the copolymerization of trivinylglycerol ether with the methyl ester of methacrylic acid. The copolymerization of trivinylglycerol ether with methacrylic acid and its methyl ester is precisely described in the experimental part. The yield and composition of the copolymers of trivinylglycerol ether and methacrylic acid (Table 1), and of methylmethacrylate (Table 2), are given. There are 2 tables and 5 Soviet references.

Card 2/3

S/062/60/000/007/014/017/XX
B004/B064

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

TITLE: Vinyl Compounds in the Diene Synthesis. Communication 3. Synthesis and Properties of the Ethers of the Series of Bicycloheptene and Di-endomethylene Octahydronaphthalene Containing Aromatic Radicals

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 7, pp. 1286 - 1290

TEXT: The present paper continues the authors' investigations on the diene synthesis by means of vinyl compounds of the $CH_2=CH-XR$ type. The authors report on the reactions of cyclopentadiene and hexachloro cyclopentadiene with vinyl-β-naphthyl-, vinylphenyl-, and vinyl-p-tert-butyl phenyl ether. The condensation of the vinyl aryl ethers with cyclopentadiene proceeds according to the scheme: (1)

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Vinyl Compounds in the Diene Synthesis. Communication 3. Synthesis and Properties of the Ethers of the Series of Bicycloheptene and Di-endomethylene Octahydronaphthalene Containing Aromatic Radicals

S/062/60/000/007/014/017/XX
B004/B064

The ratio between the forming adducts may be varied by the initial ratio of the components. As in the case of the vinyl alkyl ethers also with the vinyl aryl ethers the second stage of reaction may be carried out by means of hexachloro cyclopentadiene; ether and dihydraldine result from this reaction: (2). With hexachloro cyclopentadiene the reaction proceeds under the formation of ethers of hexachloro bicycloheptene: (3). These compounds could be easily hydrogenated on the platinum oxide catalyst; the saturated compounds of bicycloheptane or di-endomethylene-decaline resulted. The authors describe the syntheses of: III and VI (2-β-naphtho-oxy-bicyclo-(2,2,1)-heptene-5 and 1,4,5,8-di-endomethylene-2,β-naphthoxy-1,2,3,4,4a,5,8,8a-octa-hydro naphthalene) by reaction of vinyl-β-naphthyl ether with cyclopentadiene in the autoclave at 170°C; II and V (2-p-tert-butylphenoxybicyclo-(2,2,1)-heptene-5 and 1,4,5,8-di-endomethylene-2-p-tert-butylphenoxy-1,2,3,4,4a,5,8,8a-octahydronaphthalene under the

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S/062/60/000/007/014/017/XX
B004/B064

Vinyl Compounds in the Diene Synthesis.
Communication 3. Synthesis and Proper-
ties of the Ethers of the Series of
Bicycloheptene and Di-endomethylene Octahydronaphthalene Containing
Aromatic Radicals

same conditions by reacting vinyl p-tert-butyl phenyl ether with cyclo-
pentadiene. XI, X, and IX (2-β-naphthoxy-1,4,5,6,7,7-hexachloro
bicyclo-(2,2,1)-heptene-5, and 2-p-tert-butyl phenoxy-1,4,5,6,7,
7-hexachloro bicyclo-(2,2,1)-heptene-5 and 2-phenoxy-1,4,5,6,7,
7-hexachloro bicyclo-(2,2,1)-heptene-5 by reacting the corresponding
ethers with hexachloro cyclopentadiene at 110 - 120°C in the test glass
with reflux condenser. VIII (1,4,5,8-di-endomethylene-2-β-naphthoxy-
5,6,7,8,9,9,-hexachloro-1,2,3,4,4a,5,8,8a-octahydronaphthalene
(dihydraldine)) was obtained from compound III and hexachloro cyclo-
pentadiene at 120 - 135°C. Crystalline derivatives of these compounds
were obtained by means of phenyl azide. There are 2 tables and
9 references: 5 Soviet, 1 US, and 3 German.

Card 3/5

Vinyl Compounds in the Diene Synthesis Communication 3. Synthesis and Properties of the Ethers of the Series of Bicycloheptene and Di-endomethylene Octahydronaphthalene Containing Aromatic Radicals

S/062/60/000/007/014/017/XX
B004/B064

✓

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 29, 1958

Card 4/5

05000

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

5.3700 2209, 1153, 1273

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

TITLE: Synthesis of Primary γ-Organo Silicon Acetylene Alcohols

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

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

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

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

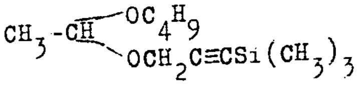
Card 1/3

85666

Synthesis of Primary γ-Organo Silicon Acetylene Alcohols

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

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



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

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

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85666

Synthesis of Primary γ-Organo Silicon Acetylene Alcohols

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

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

SUBMITTED: December 15, 1959

Card 3/3

86415
S/062/60/000/008/030/033/XX
B013/B055

53620 1153 1306 2209

AUTHORS: ~~Shostakovskiy, M. F.~~, Bogdanova, A. V., and Plotnikova, G.L.

TITLE: On the Diene Synthesis of 1,4-Dithioethyl 1,3-Butadiene With Cyclopentadiene

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 8, pp. 1514-1516

TEXT: This is a brief communication on the diene synthesis of 1,4-dithioethyl 1,3-butadiene with cyclopentadiene. The ratio of the initial substances and the time or reaction were varied in the experiments. The synthesis proceeds by stages, addition products being formed which contain varying numbers of cyclopentadiene molecules per dithioethyl-butadiene molecule. The ratio of these addition products depends on the ratio of the initial substances and duration of heating. Three addition products were separated from the reaction mixture. The first, formed by reaction of one cyclopentadiene molecule with one molecule of the diene investigated, reacted readily with an alcoholic sublimate solution with quantitative formation of ethylmercapto mercury chloride and HCl, which

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On the Diene Synthesis of 1,4-Dithioethyl 1,3-
Butadiene With Cyclopentadiene

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S/062/60/000/008/030/033/XX
B013/B055

can be easily titrated with 0.1 N NaOH. This indicates the presence of a vinylthioethyl group. (I) may therefore be assigned the structure of a 2-thioethyl 3-vinylthioethyl bicyclo(2,1,2)-5-heptene. The second product (II) contains two cyclopentadiene molecules per dithioethyl-butadiene molecule. Neither it nor the third product react with alcoholic sublimate solution. The second product may be regarded as bis[2-thioethyl-bicyclo (2,1,2)-5-heptene]. According to its composition and constants, compound (III) is [1,4,5,8-diendomethylene-2-thioethyl-3-(2'-thioethyl)-bicyclo (2',1',2')-5'-heptene]. The preparation of analytically pure samples was rendered very difficult owing to the formation of cyclopentadiene polymers which are very soluble in the addition products. The 1,4-dithioalkyl(aryl) 1,3-butadienes prepared from diacetylene, which give the typical diene reaction with maleic anhydride, exhibit dienophilic properties in the diene synthesis with cyclopentadiene. 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: January 19, 1960

Card 2/2

S/062/60/000/009/010/021
B023/B064

AUTHORS: Shostakovskiy, M. F. and Khomutov, A. M.

TITLE: Studies in the Field of the Chemical Conversions of Unsaturated and Highmolecular Compounds. Communication 15. Copolymerization of Some Divinyl Ethers With Methacrylic Acid

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 9, pp. 1681-1686

TEXT: In continuation of their previous papers (Refs. 1 and 2), the authors studied the behavior of some representatives of vinyl ethers in the copolymerization with methacrylic acid. The following two compounds were used: $CH_2 = CHOCH = CH_2$ (I), $CH_2 = CHOCH_2CH_2OCH = CH_2$ (II). The ether (I) rather tends to reactions with radical mechanism (Ref. 3). It polymerizes readily when stored and in the presence of initiators (benzoyl peroxide and dinitrile of azoisobutyric acid). The ester (II) does not polymerize under the action of the mentioned initiators, but does so

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Studies in the Field of the Chemical Conversions S/062/60/000/009/016/021
of Unsaturated and Highmolecular Compounds. B023/B064
Communication 15. Copolymerization of Some Divinyl
Ethers With Methacrylic Acid

readily in the presence of iron chloride (Ref. 4). The authors assume that these divinyl ethers, like the vinyl alkyl ethers, enter a copolymerization reaction with methacrylic acid and form acylals at the same time. The first experimental series of the copolymerization of (I) with methacrylic acid was carried out in the presence of benzoyl peroxide. At an increase of the amount of divinyl ether in the reaction medium, the copolymer yields decrease, while the number of the chain links in the ether rises (Fig. 1). The second experimental series was carried out in the presence of dinitrile of azoisobutyric acid. Fig. 1 shows the data on the dependence between yields, compositions, and molar concentration of the initial monomers. At an increase of the divinyl ether concentration in the reaction medium, the copolymer yields decrease first, then increase, and the number of the chain links of divinyl ether increases. Acylals (III) were found in the copolymer forming in consequence of competing reactions. When comparing the copolymerization of the divinyl ester with methacrylic acid in the presence of benzoyl peroxide and the dinitrile of azoisobutyric acid, the authors found that the kind of the initiator exerts a considerable

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Studies in the Field of the Chemical Conversions S/062/60/000/009/016/02
of Unsaturated and Highmolecular Compounds. B023/B064
Communication 15. Copolymerization of Some Divinyl
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influence upon the yield and the composition of the copolymers (Fig. 1). The copolymers have in both cases a three-dimensional structure and the number of the chain links of divinyl ether (I) amounts to more than 50 mole%. The vinyl alkyl ethers, forming linear copolymers with methacrylic acid, give, however, a maximum of 50 mole% of the chain links. The copolymerization under the participation of ethylene glycol divinyl ether (II) with methacrylic acid takes a course different from case (I), and is similar to the reactions with vinyl alkyl ethers. Copolymers with more than 15% chain links of divinyl ethylene glycol, have a three-dimensional structure. A relation exists between the composition of the copolymers, the yields and concentrations of the initial monomers (Ref.7). This dependence is linear (Fig. 2). The copolymers were subjected to hydrolysis to determine their composition. The content of acylals in these copolymers is considerably higher than in copolymers with (I). This may be explained by the fact that (II) tends less toward reactions of the type of a radical mechanism than (I). There are 2 figures, 4 tables, and 7 references: 6 Soviet and 1 US.

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Studies in the Field of the Chemical Conversions of Unsaturated and Highmolecular Compounds. Communication 15. Copolymerization of Some Divinyl Ethers With Methacrylic Acid

S/062/60/000/009/016/021
B023/B064

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 14, 1959

Card 4/4

SHOSTAKOVSKIY, M.F.; BOGDANOVA, A.V.; PLOTNIKOVA, G.I.; DOLGIKH, A.N.

Method of synthesizing merdaptoles and tritiated esters of orthoformic acid. Izv. AN SSSR Otd. khim. nauk no.10:1901 O '60. (MIRA 13:10)

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

(Orthoformic acid)

S/190/60/002/012/006/019
B017/B055

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

TITLE: Synthesis and Polymerization of N-Allyl Lactams

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 12, pp. 1794-1800

TEXT: The preparation and properties of N-allyl α-pyrrolidone, N-allyl ε-caprolactam and N-allyl α-piperidone are described. N-Allyl ε-caprolactam was prepared by reacting sodium derivatives of the lactams with a small excess of allyl bromide in xylene at 100-130°C. N-allyl ε-caprolactam is a very mobile liquid with a weak amine smell and a density of approximately 1. It is miscible with water, alcohol and ether. The infrared-, ultraviolet-, and Raman spectra of the compound were taken. The results are listed in Tables 1 and 2. The presence of a carbonyl group and a terminal vinyl group was established by these spectra. In their studies on radical-initiated N-allyl pyrrolidone and N-allyl caprolactam polymerization, the authors found that N-allyl lactam is not activated by benzoyl peroxide, but that 5 - 10% azodiisobutyronitrile causes stepwise poly-

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Synthesis and Polymerization of N-Allyl Lactams

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merization with formation of dimers and trimers in low yield. Table 3 gives a survey of the synthesis of N-allyl lactams. The ultimate analysis and properties of N-allyl pyrrolidone (I), N-allyl piperidone (II), and N-allyl caprolactam (III) are given in Table 4. The authors investigated the copolymerization of N-allyl pyrrolidone with vinyl acetate, methyl methacrylate and methyl acrylate, obtaining copolymer yields of up to 69%. The spectroscopic analysis was carried out by B. V. Lopatin and T. N. Shkurina, collaborators at the optical laboratory of the authors' institute. There are 6 tables and 14 references: 5 Soviet.

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

SUBMITTED: May 13, 1960

Card 2/2

5.3900

77351
SOV/79-30-1-12/78

AUTHORS: Shostakovskiy, M. F., Rabinovich, M. S., Preobrazhenskaya, Ye. V., Zykova, G. N.

TITLE: Investigation of the Synthesis of Precursors and Structural Parts of Antibiotics. I. α-Aminoadipic Acid

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 1, pp 67-71 (USSR)

ABSTRACT: The α-aminoadipic acid can be synthesized by the following two methods: (1) by condensation of γ-bromobutyronitrile with N-acetylaminomalonic ester followed by hydrolysis and decarboxylation; and (2) by amination of diethyl ester of α-bromoadipic acid with subsequent hydrolysis. The yield of α-aminoadipic acid prepared by the first and second methods is 44% (based on starting γ-bromobutyronitrile) and 82% (based on diethyl ester of α-bromoadipic acid), respectively. The technical α-aminoadipic acid is purified by dissolving in 1 N NaOH and treatment with

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Investigation of the Synthesis of
Precursors and Structural Parts of
Antibiotics. I. α-Aminoadipic Acid

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activated charcoal (pH 3.0). Upon acidification (pH 3-3.5) of the colorless filtrate crystalline α-aminoadipic acid precipitates (yield 94%), mp 173-174° (decom). Heating of diethyl ester of α-bromoadipic acid in absolute alcohol saturated with gaseous ammonia in the autoclave at 100-110° (pressure 7 atm) for 12 hr yields amide of α, α'-piperidonecarboxylic acid, mp 168-169°. When α-aminoadipic acid is recrystallized from water, about 50% of it is converted into α, α'-piperidonecarboxylic acid. Esterification of α-aminoadipic acid by heating with isopropyl alcohol in the presence of HCl yields isopropyl ester of α, α'-piperidonecarboxylic acid, mp 65.6-66.5°. This was verified by parallel synthesis of this ester from piperidonecarboxylic acid. The α-aminoadipic acid was also synthesized in the following way:

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Investigation of the Synthesis of Precursors and Structural Parts of Antibiotics. I. α-Aminoadipic Acid

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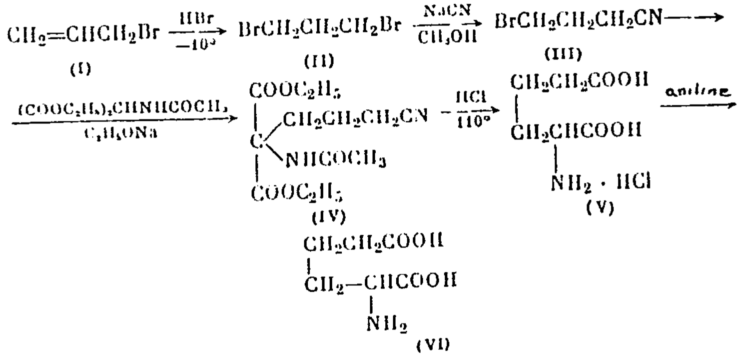
SOV/79-30-1-12/78



The authors wish to thank A. S. Khokhlov and Ye. M. Kleyner for samples of α-aminoadipic acid, and F. M. Meller for performing elemental analysis. There are 10 references, 2 Soviet, 5 U.S., 3 German. The U.S. references are: Schwenk, E., Papa, D., J. Am. Chem. Soc., 70, 3626 (1948); Bun Hof, Demorsman, J. Org. Ch., 18, 649 (1953); Waalkes, T. P., Fones, W. S., White, J.,

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Investigation of the Synthesis of Precursors and Structural Parts of Antibiotics. I. α-Aminoadipic Acid

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SOV/79-30-1-12/78

J. Am. Chem. Soc., 72, 5760 (1950); Derick, C. G., Hess, R. W., J. Am. Chem. Soc., 40, 547 (1918); Brown, G. B., Baker, B. R., Bernstein, S., Safir, S., J. Org. Ch., 12, 162 (1947).

ASSOCIATION: All-Union Scientific Research Institute of Antibiotics (Vsesoyuznyy nauchno-issledovatel'skiy institut antibiotikov)

SUBMITTED: December 29, 1958

Card 4/4

5.3900

77352
SOV/79-30-1-13/78

AUTHORS: Rabinovich, M. S., Shostakov~~ich~~skiy, M. F., Preobrazhenskaya, Ye. V.

TITLE: Investigation of the Synthesis of Precursors and Structural Parts of Antibiotics. II. Separation of α-Aminoadipic Acid Into Optically Active Forms

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 1, pp 71-75 (USSR)

ABSTRACT: Acyl derivatives were used in this work for separation of optically active forms of α-aminoadipic acid. N-benzoyl-l, d, α-aminoadipic acid, not described in literature, was synthesized in the following way: To the mixture of l, d, α-aminoadipic acid (16 g), sodium bicarbonate (90 g), and water (300 ml), after heating for 1.5 hr, add benzoyl chloride (42 g) with vigorous stirring. Continue stirring for another 4 hr, remove excess sodium bicarbonate by filtration, acidify filtrate with HCl up to ~ pH 2.0. Recrystallize the obtained acid from water, yield 18 g (68%),

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Investigation of the Synthesis of Precursors and Structural Parts of Antibiotics. II. Separation of α -Aminoadipic Acid Into Optically Active Forms

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mp 183-184°. Separation of N-benzoyl- l, d, α -aminoadipic acid into optically active forms was carried out with brucine, l -threo-1-p-nitrophenyl-2-aminopropane-1,3-diol, and d,l-threo-1-p-nitrophenyl-2-aminopropane-1,3-diol. In all cases the following optically active forms of N-benzoyl- l, d, α -aminoadipic acid were obtained: N-benzoyl- l, α -aminodipic acid, mp 177-179°, $[\alpha]_p$ + 17.2-17.3°; N-benzoyl- d, α -aminoadipic acid, mp 178-180°, $[\alpha]_p$ -16.0 to 18.6°.

The l -form of amine produces a crystalline salt of d ,N-benzoyl derivative, and the d-form, the crystalline salt of l , N-benzoylaminoadipic acid. Hydrolysis of optically active forms of N-benzoyl- α -aminoadipic acid yields l , α -aminoadipic acid, mp 184-185°, $[\alpha]_p$ +25.5° (with 1.3, 6 N HCl) and d , α -aminoadipic acid, mp 183-184°, $[\alpha]_p$ -25° (with 1.3, 6 N HCl). The authors, together with T. P. Verkhovtsevoy (VNIIA), established that the microorganism Penicillium chrysogen separates

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Investigation of the Synthesis of Precursors and Structural Parts of Antibiotics. II. Separation of α-Aminoadipic Acid Into Optically Active Forms

l, d, α-aminoadipic acid into two optically active forms. During its life it consumes only the l-form of α-aminoadipic acid. The authors succeded in obtaining d-form of α-aminoadipic acid ($[\alpha]_D$ -25.9°) from the racemate in which the above microorganism was cultivated for 5-6 days. The work devoted to the separation of racemic amino acids with optically active forms of l-threo-1-p-nitrophenyl-2-aminopropyl-1,3-diol is to be continued. The authors thank M. A. Guberniyev for his interest in this work. There are 8 references, 3 U.S., 1 German, 1 French, 1 Italian, 1 Swedish, 1 Belgian. The U.S. references are: Borsoon, H., Deasy, C. L., Haagen-Smith, A. L., et al., J. Biol. Ch., 176, 1386 (1948); Greenstein, P., Birnbaum, S. M., et al., J. Am. Chem. Soc., 75, 1994 (1953); Adams, R., Binder, L. O., J. Am. Chem. Soc., 63, 2773 (1941).

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Investigation of the Synthesis of Precursors and Structural Parts of Antibiotics. II. Separation of α-Aminoadipic Acid Into Optically Active Forms

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SOV/79-30-1-13/78

ASSOCIATION: All-Union Scientific Research Institute of Antibiotics (Vsesoyuznyy nauchno-issledovatel'skiy institut antibiotikov)

SUBMITTED: December 29, 1958

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5.3610

77353
SOV/79-30-1-14/78

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

TITLE: Reaction of Butadiyne With Amino Alcohols and Amines. I. Synthesis and Conversions of 1-(β-Diethylamino)-ethoxybut-1-en-3-yne

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 1, pp 75-81 (USSR)

ABSTRACT: Reaction of butadiyne with β-(diethylamino)-ethanol at room temperature without catalyst yields (80-90%) 1-(β-diethylamino)-ethoxybut-1-en-3-yne (I), bp 99° (11 mm), n_D^{20} 1.4832. When compound I is hydrolyzed with 10% H_2SO_4 it yields 1,3,5-triacetylbenzene (yield 80%), mp 162-163°. Reaction of compound I with aliphatic alcohols under rigorous conditions (boiling under vacuum (10 mm) for 6 hr in the presence of catalyst, potassium

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Reaction of Butadiyne With Amino Alcohols and Amines. I. Synthesis and Conversions of 1-(β-Diethylamino)-ethoxybut-1-en-3-yne

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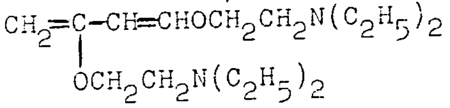
ethoxide) yields, along with the acetals of but-1-yn-4-al, also addition products of one molecule of alcohol to a molecule of ethylvinyl ether. These addition products have both a diene and an allene structure. Thus, reaction of I with β-(diethylamino)-ethanol yields (55-60%) di-(β-diethylaminoethoxy)-buta-1,3-diene (II), bp 151° (4 mm), n_D^{20} 1.4819. Compound II can also contain some 1,4-di-(β-diethylaminoethoxy)-buta-1,3-diene (IIa).



$$CH_2{=}\underset{\displaystyle OCH_2CH_2N(C_2H_5)_2}{C}{-}CH{=}CHOCH_2CH_2N(C_2H_5)_2$$

(II)

$$(C_2H_5)_2NCH_2CH_2OCH{=}CH{-}CH{=}CHOCH_2CH_2N(C_2H_5)_2 \quad \text{(IIa)}$$

Reaction of I with butanol yielded (50-60%) the acetal of but-1-yn-4-al (III), bp 138-140° (10 mm), n_D^{20} 1.4542,

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Reaction of Butadiyne With Amino Alcohols
and Amines. I. Synthesis and Conversions
of 1-(β-Diethylamino)-ethoxybut-1-en-3-yne

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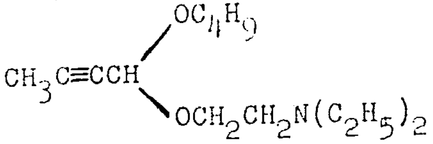
containing an admixture, a product with an allene structure. The yield of butoxy-(β-diethylamino)-ethoxybuta-1,3-diene (IV), bp 153-155° (7 mm), n_D^{20} 1.4570, in this case, was only 10-25%.



$$CH_3C{\equiv}CCH\left\langle\begin{array}{l}OC_4H_9\\OCH_2CH_2N(C_2H_5)_2\end{array}\right.$$

(III)

$$H_9C_4CCH{=}CH{-}CH{=}CHOCH_2CH_2N(C_2H_5)_2$$

(IV)

During the reaction of ethyl vinyl ether with alcohols there occurs, evidently, not only the isomerization that causes migration of the triple bond, but acetylene-allene-dienic isomerization of reaction products as well, which leads to the formation of di-alkoxybuta-1,3-dienes.

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Reaction of Butadiyne With Amino Alcohols and Amines. I. Synthesis and Conversions of 1-(β-Diethylamino)-ethoxybut-1-en-3-yne

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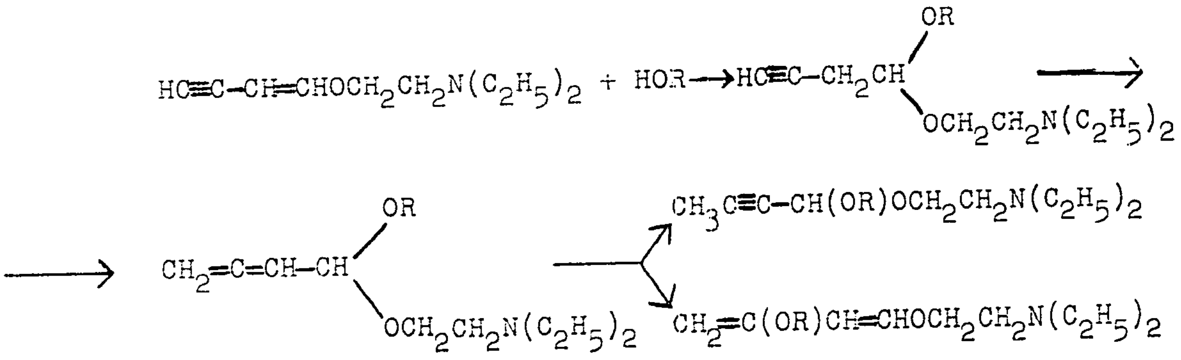
SOV/79-30-1-14/78



$R=C_4H_9$ and $CH_2CH_2N(C_2H_5)_2$

When the reaction of I with β-(diethylamino)-ethanol is extended from 6 to 22 hr, the addition product of two molecules of amino alcohol with one molecule of ethyl

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Reaction of Butadiyne With Amino Alcohols and Amines. I. Synthesis and Conversions of 1-(β-Diethylamino)-ethoxybut-1-en-3-yne

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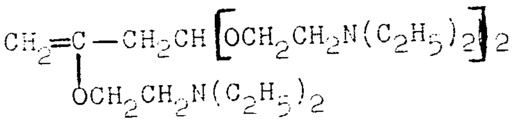
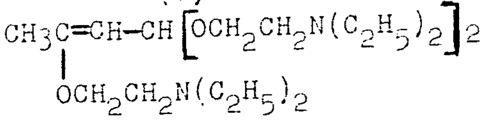
vinyl ether is obtained. The structure of this compound is V or Va (based on spectral analysis) and its physical constants are: bp 178-179°, n_D^{20} 1.4608.



$$CH_2{=}\underset{\displaystyle OCH_2CH_2N(C_2H_5)_2}{C}-CH_2CH\left[OCH_2CH_2N(C_2H_5)_2\right]_2$$

(V)



$$CH_3\underset{\displaystyle OCH_2CH_2N(C_2H_5)_2}{C}{=}CH-CH\left[OCH_2CH_2N(C_2H_5)_2\right]_2$$

(Va)

Reaction of I with ethylmercaptan at 70-80° for 6 hr yielded (60-70%) ethylmercapto-(β-diethylaminoethoxy)-

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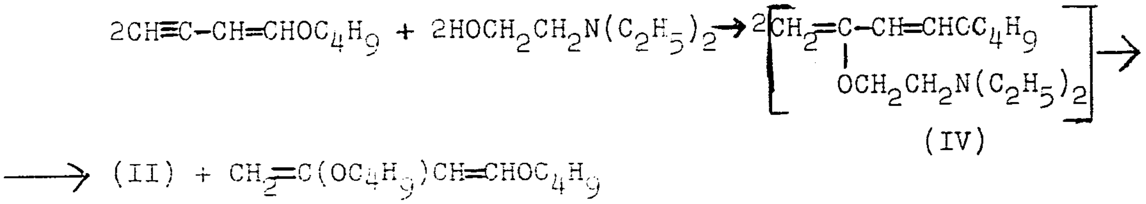
-buta-1,3-diene (VI) or (VIa), bp 152° (7 mm), n_D^{20} 1.5290. The attempt to prepare compound VI by parallel synthesis from 1-ethylmercaptobut-1-en-3-yne and 1-butoxybut-1-en-3-yne failed. Only di-(β-diethylaminoethoxy)-buta-1,3-diene (II) was obtained. The formation of II in this case can be explained by disproportionation of butoxy-(β-diethylaminoethoxy)-buta-1,3-diene (IV) into symmetric dialkoxybuta-1,3-dienes.



$$2CH\equiv C-CH=CHOC_4H_9 + 2HOCH_2CH_2N(C_2H_5)_2 \rightarrow 2\left[\begin{array}{l} CH_2=C-CH=CHCC_4H_9 \\ \qquad\;\; | \\ \qquad\;\; OCH_2CH_2N(C_2H_5)_2 \end{array}\right] \rightarrow$$

(IV)

$$\longrightarrow (II) + CH_2=C(OC_4H_9)CH=CHOC_4H_9$$

Reaction of Butadiyne With Amino Alcohols and Amines. I. Synthesis and Conversions of 1-(β-Diethylamino)-ethoxybut-1-en-3-yne

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SOV/79-30-1-14/78

The authors wish to thank B. V. Lopatin for spectral analysis of the prepared compounds. There are 11 references, 5 Soviet, 5 German, 1 U.S. The U.S. reference is: Copenhaver, J. W., Bigelon, M. H., Acetylene and Carbon Monoxide Chemistry, 305 (1949).

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

SUBMITTED: October 15, 1958

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5.3620

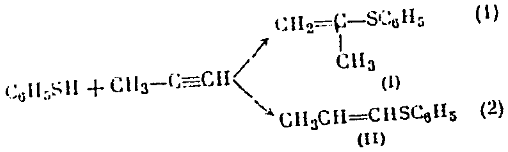
77254
SOV/79-30-1-15/78

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

TITLE: Investigation of Synthesis and Conversions of Substituted Vinyl Ethers. X. Synthesis and Conversions of Propenyl Isopropenyl Phenyl Sulfides

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 1, pp 81-86 (USSR)

ABSTRACT: Reaction of thiopenol with methylacetylene in alkaline medium yields a mixture of isopropenyl phenyl sulfide (I), bp 68-69° (6 mm), n_D^{20} 1.5690, and propenyl phenyl sulfide (II), bp 111-113° (20 mm), n_D^{20} 1.5849.



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Investigation of Synthesis and Conversions of Substituted Vinyl Ethers. X. Synthesis and Conversions of Isopropenyl Phenyl Sulfides

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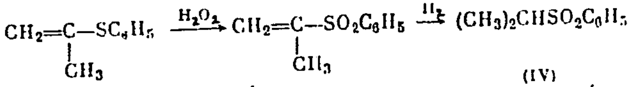
The reactions (1) and (2) are nucleophilic additions. Sterically directed addition of thiol in reaction (2) results in only one stereoisomer. This was confirmed by oxidation of propenyl phenyl sulfide yielding only one crystalline propenyl phenyl sulfone, $CH_3CH=CHSO_2C_6H_5$ (III) (yield 77%), mp 69.5-70°. Isopropenyl phenyl sulfide was converted into isopropyl phenyl sulfone (IV) for identification.



$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-SC_6H_5 \xrightarrow{H_2O_2} CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-SO_2C_6H_5 \xrightarrow{H_2} \underset{(IV)}{(CH_3)_2CHSO_2C_6H_5}$$

Oxidation of isopropenyl phenyl sulfide yields (53%) isopropenyl phenyl sulfone, bp 142° (4.5 mm), n_D^{20} 1.5470. In contrast to crystalline sulfones obtained from propenyl phenyl sulfide, the isopropenyl- and isopropyl phenyl sulfones are oil-like substances. The absorption maxima of isopropenyl phenyl and propenyl phenyl sulfides are at 1,420 cm^{-1} and 970-960 cm^{-1}, respectively. Hydrolysis of propenyl and isopropenyl

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phenyl sulfides yields propionaldehyde and acetone, respectively. Decomposition of the obtained sulfides with alcoholic solution of mercuric chloride indicated that this reaction can be used for the quantitative determination of isopropenyl phenyl sulfide only. Upon mixing of isopropenyl phenyl sulfide with a mercuric chloride solution, phenylmercuric chloride precipitates in 30 seconds and 95% HCl is recovered by titration in 24 hours. Reaction of propenyl and isopropenyl phenyl sulfides with thiophenol in the presence of a free radical catalyst yields (82%) the same compound in both cases, 1,2-diphenylmercaptopropane, $C_6H_5SCH_2CH(CH_3)SC_6H_5$ (V), bp 197-198° (7 mm), n_D^{20} 1.6218. When ethylmercaptan is used, it reacts with (I) and (II) to form compound (VI), yield 81%, bp 129-130° (5 mm), n_D^{20} 1.5715 and compound (VII), yield 82%, bp 134-135° (5 mm), 120° (3 mm), n_D^{20} 1.5725, respectively.

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Investigation of Synthesis and Conversions of Substituted Vinyl Ethers. X. Synthesis and Conversions of Isopropenyl Phenyl Sulfides

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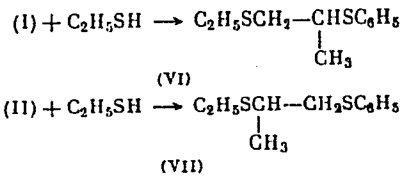


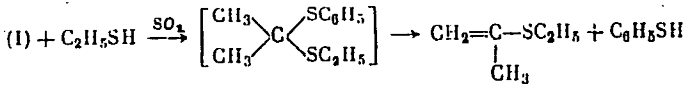
$$(I) + C_2H_5SH \rightarrow C_2H_5SCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}HSC_6H_5$$

(VI)

$$(II) + C_2H_5SH \rightarrow C_2H_5S\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2SC_6H_5$$

(VII)

Isopropenyl phenyl sulfide behaves similarly to its analog, isopropenyl phenyl ether. In the presence of catalyst (SO_2) it reacts with ethylmercaptan yielding isopropenyl ethyl sulfide, bp 112-114°, n_D^{20} 1.4755.



$$(I) + C_2H_5SH \xrightarrow{SO_2} \left[\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}SC_6H_5\\SC_2H_5\end{matrix}\right] \rightarrow CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-SC_2H_5 + C_6H_5SH$$

Hydrochlorination of isopropenyl phenyl sulfide yields α-chloroisopropyl phenyl sulfide. Since α-chloroisopropyl phenyl sulfide is an unstable compound, it was converted into tertiary-amyl phenyl sulfide, bp 96-98°

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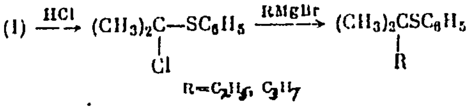
(9 mm), n_D^{20} 1.5387.



$$(I) \xrightarrow{HCl} (CH_3)_2C(Cl)-SC_6H_5 \xrightarrow{RMgBr} (CH_3)_2C(R)SC_6H_5$$

$R = C_2H_5, C_3H_7$

1,1-Dimethylbutyl phenyl sulfide (yield 19%), bp 83-84° (2 mm), n_D^{20} 1.5312, was synthesized in an analogous way. There are 16 references, 6 Soviet, 6 U.S., 1 U.K., 3 German. The 5 most recent U.S. references are: Tarbell, D. C., Lovett, W. E., J. Am. Chem. Soc., 78, 2263 (1956); Bordwell, F. G., Andersen, H. M., Pitt, B. M., J. Am. Chem. Soc., 76, 1085 (1954); Truce, W. E., Simms, J. A., J. Am. Chem. Soc., 78, 2756 (1956); Truce, W. E., Simms, J. A., Boudakian, M. M., J. Am. Chem. Soc., 78, 695 (1956); Tarbell, D. C., McCall, M. A., J. Am. Chem. Soc., 74, 48 (1952).

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ASSOCIATION: Institute of Organic Chemistry of the Academy of Sciences

5.3620

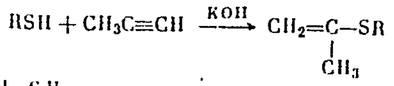
77856
SOV/79-30-2-7/78

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

TITLE: Study in the Field of Synthesis and Conversions of Substituted Vinyl Ethers. XI. Synthesis and Properties of Isopropenyl Alkyl Sulfides

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 2, pp 383-388 (USSR)

ABSTRACT: The authors synthesized isopropenyl ethyl sulfide, isopropenyl butyl sulfide and isopropenyl propyl sulfide by reacting methylacetylene with mercaptans in an alkaline medium:



$$RSH + CH_3C\equiv CH \xrightarrow{KOH} CH_2{=}C(CH_3){-}SR \qquad (I)$$

$R = C_2H_5, C_3H_7, C_4H_9.$

The reactions were performed using the method described earlier (Zhur. obshchey khim., 28, 1253 (1958)). Experimental conditions are given in Table 1.

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Table 1.

Key to Table 1. (1) Synthesized compound; (2) quantity; (3) mercaptan (in moles); (4) methylacetylene (in moles); (5) KOH (in moles); (6) dioxan (in ml); (7) conditions of reaction; (8) temperature; (9) duration of heating (in hr); (10) yields of reaction products (in %); (11) isopropenyl alkyl sulfide; (12) 1,2-dialkylmercaptopropane; (13) isopropenyl ethyl sulfide; (14) isopropenyl propyl sulfide; (15) isopropenyl butyl sulfide.

1	2				7		10	
	3	4	5	6	8	9	11	12
13	1.5	3	0.3	—	170—180°	2	44	9
14	0.47	0.94	0.09	—	110—120	1.5	49	15
15	0.34	0.68	0.068	30	120—130	1.5	51	8

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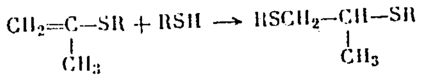
The pressure in the autoclave varied between 32 and 45 atm. (Dioxan was added to minimize tarring.) By mixing the obtained isopropenyl alkyl sulfides with additional quantities of mercaptan, the 1,2-dialkylmercaptopropanes are obtained (reaction (2)):



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}SR + RSH \longrightarrow RSCH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}SR \qquad (2)$$

$R = C_2H_5;\ C_3H_7,\ C_4H_9$

The reaction was exothermic (temperature rose to 50-60°; synthesis of 1,2-diethylmercaptopropane and 1,2-dipropylmercaptopropane). In the case of 1,2-dibutylmercaptopropane and 1-butyl-mercapto-2-ethylmercaptopropane, the mixture had to be heated to 80° in presence of 0.01 g of azoisobutyronitrile. Table 2 gives the yields and physical constants of the synthesized compounds.

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Table 2.

1	2	3	n_D^{20}	d_4^{20}	MR_D		4 (%)			6	5 (%)		
					4		C	H	S		C	H	S
7	44	114–115 (750)	1.4750	0.8720	32.99	32.86	58.75, 58.92	9.92, 9.89	31.16, 31.07	$C_5H_{10}S$	58.75	9.87	31.38
[illegible]	49	47–48 (25)	1.4740	0.8988	37.61	37.48	62.11, 62.13	10.65, 10.57	27.45, 27.55	$C_6H_{12}S$	62.01	10.40	27.57
7	51	66–67 (25)	1.4730	0.8846	42.21	42.10	64.63, 64.58	10.84, 10.95	24.68, 24.81	$C_7H_{14}S$	64.52	10.82	24.60
[illegible]	84	112–113 (26)	1.5033	0.9632	50.16	50.37	51.10, 51.10	9.80, 9.82	38.74, 38.58	$C_7H_{16}S_2$	51.18	9.82	39.04
11	90	134–135 (25)	1.4963	0.9408	59.74	59.70	56.42, 56.51	10.57, 10.52	33.17, 33.08	$C_9H_{20}S_2$	56.46	10.48	33.34
[illegible]	85	114–115 (3.5)	1.4920	0.9253	69.10	68.84	59.69, 59.70	10.97, 10.93	29.01, 28.96	$C_{11}H_{24}S_2$	59.94	11.0	29.10
[illegible]	72	89–90 (3)	1.4965	0.9408	59.74	59.70	56.41, 56.17	10.62, 10.41	33.03, 32.98	$C_9H_{20}S_2$	59.16	10.48	33.34

* In calculation of MR_D the authors have used atomic refraction of sulfur, found for diallyl sulfide by T. S. Prise and D. F. Twiss (J. Chem. Soc., 101,

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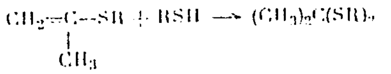
1259 (1912)) and equal to 8.04.
**Atomic refraction of sulfur was taken as equal to 7.921 (Vogel, A. I., J. Chem. Soc., 1948, 1820).

In acid medium isopropenyl alkyl sulfides react with mercaptans (after dropwise addition of isopropenyl alkyl sulfide to equimolar quantity of mercaptan containing 5-8 drops of HCl, the mixture was heated to 50° for 5 min and left overnight; it was then neutralized, dried over K_2CO_3, and distilled) by an ionic mechanism, the reaction obeying Markownikoff's (Markovnikov's) rule, yielding 2,2-dialkylmercaptopropanes:



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}SR + RSH \longrightarrow (CH_3)_2C(SR)_2 \qquad (3)$$

The 2,2-dialkylmercaptopropanes decompose on heating into the initial compounds. Passing hydrogen chloride

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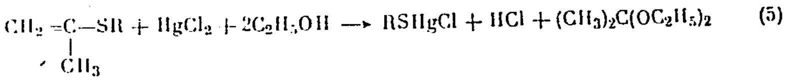
through isopropenyl alkyl sulfides at -20° resulted in formation of α-chloroisopropyl alkyl sulfide, which easily decomposes on raising temperature to 0°, giving off HCl and a complex mixture of products. Acid hydrolysis of isopropenyl alkyl sulfides yields acetone as one of the products. Quantitative decomposition of isopropenyl alkyl sulfides and 2,2-dialkylmercaptopropanes by excess of alcoholic solution of mercuric chloride (reaction 5)(with subsequent titration of HCl by NaOH):



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}SR + HgCl_2 + 2C_2H_5OH \longrightarrow RSHgCl + HCl + (CH_3)_2C(OC_2H_5)_2$$ (5)

can be used for estimation of purity of these compounds. In the case of sulfides, the reaction mixture (0.1-0.2 g of sulfide and 5 ml of 20% solution of $HgCl_2$ in alcohol) was heated at 70° in a sealed ampoule for 3 hr, transferred quantitatively into a flask, and

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titrated with 0.1N NaOH to methylorange end point. In the case of 2,2-dialkylmercaptopropanes, the reaction mixture (7 ml of $HgCl_2$ solution was used for 0.1-0.2 g sample) was simply left overnight in a stoppered conical flask. There are 3 tables; and 12 references, 2 Soviet, 4 German, 2 U.K., 3 U.S., 1 Polish. The U.S. and U.K. references are: P. I. Wiezewich, L. B. Turner, P. K. Florich, Ind. Eng. Ch., 25, 295 (1933); U.S. Patent 2066191, Ch. A., 31, 1038^4 (1937), Ch. S., 32, 8359 (1938); T. S. Prise, D. F. Twiss, J. Chem. Soc., 101, 1259 (1912); A. I. Vogel, J. Chem. Soc., 1948, 1820; F. L. Cairus, G. L. Evans, A. W. Larchar, B. C. McKusick, J. Am. Chem. Soc., 74, 3988 (1952); T. C. Whitner, E. E. Reid, J. Am. Chem. Soc., 43, 639 (1921).

SUBMITTED: February 20, 1959

Card 8/8

S/079/60/030/04/13/060
B001/B016

5.3831

AUTHORS: Shostakovskiy, M. F., Prilezhayeva, Ye. N., Azovskaya, V. A., Dmitriyeva, G. V.

TITLE: Investigations in the Field of Sulfones and Sulfoxides. I. Synthesis of Vinyl Ethyl Sulfone and Some of Its Transformations

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 4, pp. 1123-1130

TEXT: The data available on the reactivity of low vinyl alkyl sulfones (Refs. 1-10) under the influence of ionic and free-radical initiators are not clear. In order to clarify this problem, vinyl ethyl sulfone was taken as initial product. It was synthesized by dehydration of 2-hydroxy-diethyl sulfone (I) with phosphoric acid at $260-270^0$ in the vacuum (Ref. 11) according to the scheme

$$HOCH_2CH_2SC_2H_5 \xrightarrow{H_2O_2} \underset{(I)}{HOCH_2CH_2SO_2C_2H_5} \xrightarrow{H_3PO_4} \underset{(II)}{CH_2{=}CHSO_2C_2H_5}.$$

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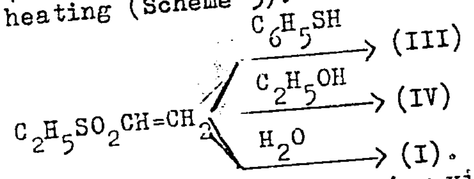
80794

S/079/60/030/04/13/080
B001/B016

Investigations in the Field of Sulfones and Sulfoxides. I. Synthesis of Vinyl Ethyl Sulfone and Some of Its Transformations

The yield in pure sulfone (II) was 70-75%; it contained no sulfoxides. The dehydration method is far more convenient than the widely used dehydrochlorination method (Refs. 1,2a,3,4,6,10) (Scheme 2). "Triton B" was used as the initiator of the ionic reactions of vinyl ethyl sulfone (II); the reaction proceeded smoothly and quantitatively on intense heating (Scheme 3):



The attempt of polymerizing vinyl ethyl sulfone under the influence of free-radical initiators gave polymers in fair yield on prolonged heating (Polymerization Schemes). Vinyl ethyl sulfone shows a high dienophilic activity, and yields adducts with cyclopentadiene, hexachloro cyclopentadiene, and chloroprene. The table shows the polymerization of vinyl ethyl sulfone at 60° for 60 h. There are 1 table and 20 references, 4 of which

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Investigations in the Field of Sulfones and Sulfoxides. I. Synthesis of Vinyl Ethyl Sulfone and Some of Its Transformations

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are Soviet.

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

SUBMITTED: June 22, 1959

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SHOSTAKOVSKIY, M.F.; GUSEYNOV, I.I.; VASIL'YEV, G.S.

Synthesis of compounds of the type of 1-alkylthio-2-oxychlorophosphine-3-chloro-1,3-butadienes. Zhur. ob. khim. 30 no.9:2832-2835 S '60.
(MIRA 13:9)

1. Institut organicheskoy khimii Akademii nauk SSSR.
(Butadiene)