Investigations in the Field of the [illegible]
XCIX. On the Problem of the Synthesis of [illegible]
of Isoprene With Its 1,4-Hydrochloride

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Lenin-
grad Technological Institute imeni Lensovet)

SUBMITTED: May 31, [illegible]

Card [illegible]/3

AUTHORS: Petrov, A. A. [illegible]

TITLE: Investigations [illegible] Systems [illegible]
v oblasti [illegible] [illegible]
Bromine [illegible]
bromo [illegible] butenine

PERIODICAL: Zhurnal [illegible]
[illegible] 19[illegible] (USSR)

ABSTRACT: Already earlier the authors [illegible]
of vinyl [illegible]
group, and [illegible]
and the [illegible]
bond, the [illegible] the [illegible] vinyl [illegible]
tylene on the triple [illegible] position [illegible]
deviations in the [illegible]
shifting of the electron [illegible]
the influence of the [illegible] whereas in the first [illegible]
the double bond and in the latter case the triple [illegible]
vated. It was of interest to compare these data with the data
of the bromine addition to the [illegible] derivatives of vinyl
acetylene built up by different ways. For this purpose the

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Investigations in the field of [illegible]
On the Addition Order of Br[illegible] [illegible]

addition order of the first bromine [illegible] is [illegible] phenyl-substituted vinyl acetylenes was determined [illegible] buten-3-in-1 (I) and on 1-phenyl [illegible] (II). The corresponding data were so far not availa[illegible] apart from the addition [illegible] hydrocarbons under formation of [illegible] tetrabromides [illegible]. In order to avoid the isomerization and polymerization of the dibromides by heating, they were not separated in a pure state from the solutions. The determination of the structure of the dibromides was carried out on the basis of a comparison of the infrared spectra of the hydrocarbon solutions (I) and (II) in CCl_4 with those of the solutions of the [illegible] which were brominated in the [illegible] solvent with [illegible]. It was previously [illegible] that the infrared [illegible] an exact determination of the structure [illegible] of the halogens [illegible] the vinyl acetylene [illegible] tion order of [illegible] phenyl-vinyl [illegible] I and II was thus determined [illegible]. The [illegible] spectroscopic [illegible] (see the figure and [illegible]).

Card [illegible]

Investigations in the Field [illegible]
3. On the Addition Order [illegible] es

[illegible] vi [illegible]
shifting formulae I [illegible] II [illegible]
carbon atom [illegible]
are [illegible] figure [illegible]

ASSOCIATION: Leningradskiy tekh [illegible] institut [illegible]
[illegible] Techn [illegible]

SUBMITTED: May [illegible], [illegible]

Card 3/3

SOV/7[illegible]/[illegible]

(5)

AUTHORS. Petrov, A. A., Bal'yan, Kh. V.,
Kheruze, Yu. I., Yakovleva, T. V.

TITLE. The Article is Open for Discussion (V poryadke diskussii).
On the Question of the Character of Chloroarylation of Vinyl
Acetylene (K voprosu o poryadke khloraarilirovaniya vinil
atsetilena

PERIODICAL: Zhurnal obshchey khimii, 19[illegible], Vol [illegible], Nr [illegible], pp [illegible] - [illegible]
(USSR)

ABSTRACT: The data of the American patent 2[illegible]244 according to which
vinyl acetylene is chloroarylized with diazo salts only on the
ethylene bond (I) have been confirmed in the recently publish-
ed report of A. V. Dombrovskiy (Ref 1). The exclusively claim-
ed 1,2-affiliation of chlorine and aryl in this radical proc-
ess seemed to the authors not quite probable. The frequently
repeated analysis under conditions proposed by Dombrovskiy
showed, that the categoric conclusion of this author with re-
gard to the character of chloroarylation of vinyl acetylene
does not correspond to reality. In every case the reaction
takes place under formation of somewhat varying, but always
considerable quantities of 1,4-products (20-40% of all adducts).

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The authors gained this conviction on the basis of the analyses of infrared spectra of the adducts. In addition to the frequencies of the acetylene group the spectra contained in the final phase an intensive frequency which could only be attributed to the allene group of the compound (II). The chloroarylation products of the vinyl acetylene apparently contain in very small quantities also a third isomer, the 1,3-diene isomer (III) because the spectrum of the product in the range [illegible] cm^{-1} shows a small maximum, which is characteristic of the group $CH_2=$.

According to Dombrovskiy's report phenyl-vinyl acetylene to which 20% allene chloride is admixed, is obtained at the dehydro-halogenation of chloroarylation products of the vinyl acetylene. Accordingly this allene chloride contains a much less mobile chloride atom, than the acetylene chloride (I). To produce pure phenyl-vinyl acetylene, the method of S. N. Reformatskiy (Ref 5) was used and this reaction was accompanied by a partial propargyl re-grouping and the formation of a mixture of approximately 80% (IV) and 20% (V). The chloride (VI), however, which was obtained from this mixture by the re-

The Article is Open for Discussion. On the Question of the Character of Chl[illegible] of Vinyl Acetylene

[illegible]

action of $SOCl_2$ contains a very small quantity of allene chloride. The same happens when phenyl-vinyl acetylene is obtained at the dehydrohalogenation of chloride (VI). The data obtained are shown in the table and in the diagram. There are [illegible] figure and [illegible] references, [illegible] of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Technological Institute imeni Lensoveta)

SUBMITTED: July [illegible]

Card 3/3

5 (3)

AUTHORS: Al'bitskaya, V. M., [illegible], Ye. I., [illegible]
Petrov, A. A., Yakovleva, T. V.

TITLE: Investigations in the Field of Conjugate Systems (Issledovaniya v oblasti sopryazhennykh sistem). [illegible]. Oxidation of Vinyl Alkyl Acetylenes With Benzoyl Hydroperoxide ([illegible]. Okisleniye vinilalkilatsetilenov gidroperekis'yu benzoila)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp [illegible]

ABSTRACT: In the papers of some authors (Refs 1, 2) it was shown that in the case of oxidation of vinyl acetylene hydrocarbons with hydroperoxides the affiliation of oxygen first takes place to the ethylene bond under formation of acetylene monoxides only. In the above papers only compound vinyl acetylene or diene hydrocarbons were used but no simple ones. The authors tried to oxidize the vinyl ethyl- and vinyl butyl acetylene with benzoyl hydroperoxide in the work under review. It was interesting to find that the authors had great difficulties in experimenting the production of pure oxides of superior vinyl alkyl acetylenes by bromhydrins, because the poor solubility of bromhydrins in water did not permit the separation of the latter from dibromides by means of extraction with water. In the case

Card 1/3

[illegible]

Investigations in the Field of Conjugated Systems. CI. Oxidation of Vinyl Alkyl Acetylenes With Benzoyl Hydroperoxide

of oxidation of both hydrocarbons acetylene oxides were obtained. The vinyl ethyl acetylene oxide has [illegible] constants nearly equal to the oxide of the same composition which was obtained earlier by means of [illegible] (Ref. 7). To get more certainty about this infra-red spectra of the vinyl acetylene oxides were taken. The [illegible] of the [illegible] obtained showed that in both cases [illegible] exist. The spectrum of the oxide obtained by oxidation of the hydrocarbon differed from the same oxide that [illegible] over bromhydrin, only by the presence of the [illegible] cm^{-1} of mean intensity (Figure). This frequency also appears in the spectrum of the diene oxides which are obtained in the same way. On the whole the spectra of the vinyl butyl acetylene and the vinyl ethyl acetylene are similar. On the basis of the results of the spectroscopic investigation it was shown that in the case of vinyl ethyl acetylene the affiliation of oxygen at the oxidation with benzoyl hydroperoxide first of all takes place on the ethylene bond. In the case of vinyl butyl acetylene it can be said with reservation only that this orientation predominates. There are 1 figure and 7 references.

Card 2/3

Investigations in the Field of Conjugated Systems. [illegible]
CI. Oxidation of Vinyl Alkyl Acetylenes With Benzoyl Hydroperoxide

4 of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta
(Leningrad Technological Institute imeni Lensovet)

SUBMITTED: June 18, 1958

Card 3/3

SOV/79-[illegible]

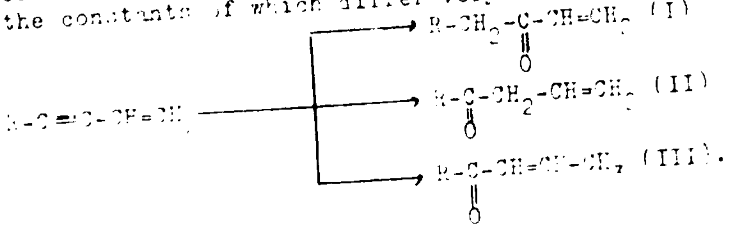
5 (3)

AUTHORS: Kupin, B. S., Petrov, A. A.

TITLE: Investigations in the Field of Conjugate Systems (Issledovaniya v oblasti sopryazhennykh sistem). CII. On the Direction of Hydration of Vinyl Alkyl Acetylenes (CII. O napravlenii gidratatsii vinilalkilatsetilenov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol [illegible], Nr [illegible] pp [illegible] (USSR)

ABSTRACT: In the present paper the hydration of vinyl methyl-, vinyl ethyl-, vinyl propyl- and vinyl butyl acetylene was carried out in the presence of mercury combined with sulfuric acid. In each case the formation of three isomeric ketones could be expected, the constants of which differ very abruptly:



$$R-C\equiv C-CH=CH_2 \rightarrow \begin{cases} R-CH_2-\overset{\overset{O}{\|}}{C}-CH=CH_2 & (I) \\ R-\underset{\underset{O}{\|}}{C}-CH_2-CH=CH_2 & (II) \\ R-\underset{\underset{O}{\|}}{C}-CH=CH-CH_3 & (III). \end{cases}$$

Thus, however, alkyl propenyl ketones (III), with admixed alkyl

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Investigations in the Field of Conjugate Systems. [illegible]
CII. On the Direction of Hydration of Vinyl Alkyl Acetylenes

alkyl ketones (II) were mainly obtained. The structure of the ketones was determined by comparison of their constants and infrared spectra (Figure), by means of publication data as well as by investigation of the saturated ketones forming from them by hydrogenation. The constants and infrared spectra of the synthesized methyl-propenyl-, ethyl-propenyl- and propyl-propenyl ketones are closely related to those given in publications (Refs 11, 12). In all spectra the grouping -CH=CH- was proven by the intensive frequencies in the range of 970 cm^{-1}. The hydrogenation of all hydration products over Pd/CaCO, mainly

led to the alkyl propenyl ketones described in publications (Ref 12). The affiliation rate of water decreases with the enlargement of the hydrocarbon radical, which caused that the reaction be carried out at heating. The manner of affiliation of water and alcohols to the vinyl alkyl acetylenes according to reference 14 does not correspond to the manner of affiliation of hydrogen halides, which may base on the fact that these reactions take place differently. There are 1 figure and 16 references, 11 of which are Soviet.

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Investigations in the Field of Conjugate Systems. [illegible]
CII. On the Direction of Hydration of Vinyl Alkyl Acetylenes

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta
(Leningrad Technological Institute imeni Lensoveta)

SUBMITTED: June 18, 1958

Card 3/3

5 (3)

AUTHORS: Petrov, A. A., Karetina, [illegible] [illegible]

TITLE: Letter to the Editor (Pis'mo v redaktsiyu). Addition of Amines to Diacetylene (O prisoyedinenii aminov k diatsetilenu)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, p 2458 (USSR)

ABSTRACT: Some publications are available on the investigation of the reactions of diacetylene with nucleophilic compounds (Refs [illegible]). But only brief data are published with respect to the addition of amines to the diacetylene without detailed characterization of the resulting products (Refs 1, 4). The authors found that diacetylene adds the dimethyl and diethylamine in benzene solution already at low temperatures and without catalysts to give the tertiary vinyl-acetylamines. The structure of these amines was confirmed by their infrared spectra. Intense frequencies of the conjugated vinyl-acetyl grouping

$-CH = CH - C \equiv CH$ were found in them ([illegible], 3288 cm^{-1}). The amines synthesized are colorless liquids which rapidly turn brown on standing and corrode the [illegible]. [illegible] diethylamino-butenine, dissolved in CCl_4, [illegible] the first [illegible]

Card 1/2

Letter to the Editor. Addition of Amines to Diacetylene [illegible]

molecule at the triple bond, thus forming the [illegible], in the infrared spectrum of which the frequencies of the [illegible]-diene grouping are found and the frequencies of the triple bond are nearly absent. There are 4 references, [illegible] of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Technological Institute imeni Lensovet)

SUBMITTED: March 28, 1959

Card 2/2

AUTHORS	Petrov, A. A., Bal'yan, Kh. V. SOV/[illegible] Bunina-Krivoruchko, L. [illegible] Yak[illegible], T. V.
TITLE	Inv[illegible]ations in the F[illegible] of Conjugate Systems [illegible] zation of Divinyl With the Hydr[illegible] ride of [illegible] [illegible] Dichlor[illegible]butene
PERIODICAL	Zhurnal [illegible] khimii, [illegible], Vol [illegible], Nr [illegible], pp [illegible] (USSR)
ABSTRACT	In their report (Ref [illegible]) A. L. Klebanskiy, [illegible] and N. G. Barkhudaryan recently asserted that [illegible] [illegible] [illegible] with divinyl only the [illegible] [illegible]. To solve this problem [illegible] with divinyl under standard [illegible] presence of [illegible] chloride (Refs [illegible]) was [illegible] the present paper. The results [illegible] [illegible] obtained by Klebanskiy and [illegible] [illegible] [illegible] [illegible] [illegible] at [illegible] mm Hg [illegible] Klebanskiy [illegible] almost equal quantities were obtained [illegible]
Card 1/[illegible]	

Investigation in the Field of Conjugate Systems. S [illegible]
CV. Telomerization of Dienes With the Hydrochloride
of Chloroprene [illegible] dichlorobutene [illegible]

tillation the first predominantly containing the [illegible] adduct [illegible] dichlorooctadiene [illegible] and the second predominantly the [illegible] adduct [illegible] dichlorooctadiene [illegible] From [illegible] the same aldehyde [illegible] octadiene [illegible] was [illegible] according to the spectrum and melting point of the [illegible] phenyl hydrazone by way of the Sommelet reaction [illegible] spectrum of this aldehyde one intense frequency [illegible] the carbonyl group and two frequencies to the group [illegible] CH=CH. According to the spectrum the distillate [illegible] of both fractions appears to be a [illegible] product which [illegible] cally free of the [illegible] adduct but contains [illegible] bonyl compounds. From the hydrogenation of the [illegible] $C_8H_{12}Cl_2$ over Pd/CaCO$_3$ the [illegible] octane resulted which was [illegible] fied. Thus, it was shown that in contrast to data [illegible] and collaborators [illegible] dichlorobutene as well as [illegible] ide adds to divinyl [illegible] the positions [illegible] and [illegible] significant differences exist between the adducts [illegible]

Card 2/3

Investigations in the Field of Conjugate Systems. SOV/79-[illegible]
[illegible] Telomerization of Divinyl With the Hydrochloride
of Chloroprene (1,3-Dichlorobutene-2)

the higher telomers. The product obtained by Klebanskiy and collaborators corresponds to that obtained by the authors exactly according to their instructions, however its yield is considerably smaller than that mentioned in their report. Besides, a carbonyl compound is admixed to this product, probably a ketone as a result of a hydrolytic cleavage of the chlorine atom from the double bond. There are 1 figure and 9 references, 8 of which are Soviet.

ASSOCIATION Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Institute of Technology imeni Lensovet)

SUBMITTED July [illegible]

AUTHOR: [illegible]

TITLE: [illegible]

PERIODICAL: [illegible]

ABSTRACT: [illegible] derivatives, [illegible] this [illegible] hydrocarbons and their [illegible] were investigated by the [illegible] transconfiguration. [illegible] in which the [illegible]

Card 1/2

Dipole Moments and Activity [illegible] in the Telomerization Reaction [illegible] With [illegible] Hydrocarbons. [illegible] Alkyl Chlorides

therefore, [illegible] corresponding telomers were [illegible] with [illegible]ation. By determining the dipole moments of the [illegible] chlorides investigated and [illegible] allyl chloride the following conclusions were drawn: 1) Allyl halogen derivatives exhibit somewhat lower dipole moments, as compared to their corresponding saturated analogues (Ref [illegible]). 2) Dipole moments of allyl halogen derivatives grow with increasing number of methyl groups on the double bond. 3) To a somewhat weaker degree, the dipole moments act upon the methyl groups at the carbon bound with chlorine. 4) A second chlorine atom at the double bond somewhat increases the moment. These and further investigation results and conclusions showed that the peculiarities in the behavior of halogen derivatives, in the telomerization with ethylene, are not only determined by their dipole moments and the moments of telomers. Thus, there is no direct relation between reactivity properties and dipole moments. There are [illegible] tables, [illegible] references, 7 of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Institute of Technology imeni Lensovet)

SUBMITTED: July [illegible], 1958

Card 2/2

5(3)

AUTHORS: Petrov, A. A., Porfir'yeva, Yu. I. SOV/79-[illegible]

TITLE: Investigations in the Field of Conjugate Systems. CVII. On the Affiliation Order of Iodine Chloride to the Vinyl Acetylene Hydrocarbons

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol [illegible], Nr [illegible], pp 193[illegible] - [illegible] (USSR)

ABSTRACT: The authors continued their investigation of the rules governing the reactions of vinyl acetylene hydrocarbons with halogens (Refs 1-4), and caused them to react with iodine chloride. Affiliation of iodine chloride to vinyl acetylene yielded two fractions having the composition C_4H_4ICl, differing sharply from each other as to boiling temperatures and other properties. The low-boiling product proved to be very stable against the action of alcoholic caustic lyes. Its infrared spectrum revealed the characteristic frequencies of the conjugate system of double bonds, vinyl group, terminal methylene group, terminal acetylene group. These data point to compound (I) which is mixed with compound (II). The prevailing high-

Card 1/2

Investigations in the Field of [illegible] XVII. S[illegible]
On the Affiliation Order of Iodine [illegible] Vinyl Acet[illegible]
carbons

b[illegible] it has [illegible]
[illegible]
revealed [illegible]
frequencies [illegible]
mixture [illegible] very [illegible]
in [illegible] (III). Thus, vinyl acetylene [illegible]
chlorine [illegible]
as is [illegible]
investigat[illegible]. The authors [illegible]
[illegible] and vinyl alkyl [illegible] (formulas IV-IX). It was [illegible]
addition [illegible] in all cases [illegible]
as in the addition [illegible] vinyl [illegible]
yield [illegible] adducts [illegible]
acetylenes and [illegible]; vinyl alkyl
ethylene [illegible], the latter [illegible] with an admixture of [illegible]
diene iodine [illegible]. Chlor vinyl [illegible] and [illegible]
acetylenes [illegible]
on the [illegible] of vinyl alkyl [illegible]. The
differences in the affiliation of iodine [illegible] to the vinyl

Card 2/3

Investigations in the [illegible] XVII. [illegible]
on the Annihilation [illegible]
[illegible]ons [illegible]

[illegible] 33 [illegible]

ASSOCIATION: [illegible]

SUBMITTED: July [illegible]

Card [illegible]

5(3)

SOV/[illegible]

AUTHORS: ~~Petrov, A. A.,~~ Kupin, B. S.

TITLE: Letter to the Editor. On the Hydration Order of [illegible] Doubly Substituted Acetylenes

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 3153 - 3154 (USSR)

ABSTRACT: The monosubstituted acetylene hydrocarbons, among them also alkenyl acetylenes, result in methyl-alkyl- (or alkenyl)-ketones only when hydrated under the reaction conditions suggested by Kucherov (Refs 1-3). Accordingly, vinyl-alkyl acetylenes should result in alkyl-vinyl ketones, however, they add water quite irregularly under the formation of alkyl propenyl ketones. On the basis of theoretical considerations, this order of hydration can neither be explained by the 1,4-addition of water nor by polarization of the molecules of vinyl-alkyl acetylene under the influence of radicals. To find the causes for the hydration direction of vinyl- and divinyl acetylene, the direction in which water is added to the simplest methyl-alkyl acetylenes was investigated by Kucherov's reaction. Comparable data on these problems have not yet been dealt with in publications. The composition of the ketone mixtures was

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Letter to the Editor. On the Hydration Order of Unsymmetri- S/079/[illegible]
cal Doubly Substituted Acetylenes

determined by comparing the intensity of the characteristic frequencies in the infrared spectra of the hydration products to that in spectra of artificial mixtures with a known content of each of the expected ketones. The results are indicated in the table. Thus, the dependence of the order of hydration upon the structure of the radicals is proved. There are [illegible] and 5 references, [illegible] of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta
(Leningrad Technological Institute imeni Lensovet)

SUBMITTED: May 25, 1959

Card 2/2

5(3)

AUTHORS: Petrov, A. A., Kormer, V. A. SOV/[illegible]

TITLE: On the [illegible] of Lithium Ethyl and Lithium Butyl with Vinyl-alkyl Acetylenes (O prisoyedinenii litiy-etila i litiy-butila k vinilalkilatsetilenam)

PERIODICAL: Doklady Akademii nauk SSSR, [illegible], Vol [illegible], Nr [illegible], pp 1041-1043 (USSR)

ABSTRACT: There are only few data available [illegible] combination of lithium-organic compounds to carbon [illegible] bonds (Refs 1 - 3). Monomeric [illegible] products [illegible] only by aryl-olefines. The radical reacts here with the [illegible] substituted final carbon atom. If lithium-organic compounds act upon olefines and diolefines, a telomerization takes [illegible]. However, substances can be isolated from the re[illegible] after the hydrolysis or after the treatment with C[illegible] wh[illegible] according to their composition, correspond [illegible]. In the case of diolefines the [illegible] apparently occurs according to the same rule [illegible] adducts have here, however, apparently a [illegible]. Accordingly, a further telomerization yields [illegible]

Card 1/3

On the Combination of Lithium Ethyl and Lithium [illegible]
Butyl with Vinyl-alkyl Acetylenes

with a normal and with an isostructure [illegible] the latter is favored by a temperature [illegible] of the authors showed that vinyl alkyl [illegible] with lithium ethyl and lithium butyl a[illegible] with the formation of hydrocarbons C_nH_{2n-2} [illegible] residue (Table 1). Figure [illegible] shows the infrared [illegible] the hydrogenation products (recorded with [illegible] Yakovleva). They proved [illegible] identical [illegible] n heptane and n octane. Hydrocarbons [illegible] were obtained by hydrolysis and [illegible] further adducts. Thus, it was detected [illegible] vinyl-alkyl acetylenes [illegible] lithium atom migrates to the triple bond [illegible] lithium-organic compounds with one [illegible] bond are produced in the course of [illegible] compounds with a triple bond would [illegible] the polymers. However, no frequencies of a tr[illegible] detected in the infrared spectrum of the [illegible] The frequency of a double bond [illegible] in the [illegible]

Card 2/3

On the Combination of Lithium Ethyl and Lithium Butyl to Vinyl-alkyl Acetylenes 30[illegible]

apparently in the grouping -CH=CH-, since a dense absorption takes place within the range of [illegible] frequencies at [illegible] cm^{-1}. The last-mentioned grouping is most likely to be formed by the isomerization of the Allen system in the polymer. The above-discussed reaction is a new method of producing the least accessible and investigated group of Allen hydrocarbons with almost any desired position of the Allen group in the middle of the carbon chain. There are [illegible] figure, [illegible] table, and [illegible] references, [illegible] which are Soviet

ASSOCIATION: Leningradskiy tekhnologicheskiy institut im. Lensoveta (Leningrad Institute of Technology imeni Lensovet)

PRESENTED: December 11, 1958, by B. A. Arbuzov, Academician

SUBMITTED: November 24, 1958

Card 3/3

5 (2,3)

AUTHORS: Petrov, A. A., Kormer, V. A. SOV/20-126-[illegible]

TITLE: On the Addition of Lithium Diethyl and Lithium Dibutyl Amide to Vinyl Acetylene and to Vinyl Alkyl Acetylenes (O prisoyedinenii litiydietil- i litiydibutilamidov k vinilatsetilenu i vinilalkilatsetilenam)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 6, pp 1278 - 1281 (USSR)

ABSTRACT: Only few data are available in publications concerning the subject mentioned in the title (Refs 1-3). In the present paper it is proved that the adducts of amines (diethyl and dibutyl amines) to vinyl acetylene hydrocarbons form by treating the addition products of the lithium dialkyl amides to these hydrocarbons with water. The mentioned alkyl diamides react at room temperature and under normal pressure. This reaction has hitherto not been described. According to the nature of vinyl acetylene hydrocarbon and the amide various products form from the corresponding reaction. Vinyl acetylene forms amines (III) with an acetylene end group (in the case of diethyl amine with a 20% yield) without any side processes. Besides polymers (25-30% vinyl methyl acetylene produces mainly the dimer (IV) with a

Card 1/3

On the Addition of Lithium Diethyl and Lithium Dibutyl Amide to Vinyl Acetylene and to Vinyl Alkyl Acetylenes

SOV/20-126-6-37/[illegible]

yield of approximately 40%. Amines form only in very low yields (5%); they have different structure according to the nature of the amide. In the case of the addition of lithium diethyl amide an amine forms with an acetylene end group (V); in the case of the lithium dibutyl amide an allene amine compound (V) is formed (see scheme). Vinyl ethyl acetylene furnishes allene amines of the type (VI) with lithium dialkyl amides (45-55%). The dimer amount does not surpass 10%. The structure of the amines was determined above all by their infrared spectra (Fig 1). Identities with already known substances were found in this connection (Ref 4). Moreover, the structure of the amines was determined by hydrogenation on colloidal palladium (Ref 5). In the infrared spectrum of the dimer of vinyl methyl acetylene

the absorption in the range of from 964 cm^{-1} indicates that the double bond is formed by a —CH═CH— group (Fig [illegible]). According to all these data the dimer may be ascribed the formula: 6-methyl-nonene-3-diine-1,8 (VI). The dimer of vinyl ethyl acetylene has an analogous structure. It is most probable that the

On the Addition of Lithium Diethyl and Lithium Dibutyl Amide to Vinyl Acetylene and to Vinyl Alkyl Acetylenes

SOV/20-126-6-37/6

dimers form due to the addition of their metallization products to vinyl acetylenes. In this connection the multiple bonds are shifted to the end of the chain under the effect of the lithium dialkyl amides. Table 1 gives the constants of the produced substances. Thus, it was found that lithium dialkyl amides may be added to the vinyl acetylenes similar to the lithium alkyls the radical enters position 4 (Ref 7). In both cases the reaction probably takes place according to the radical mechanism. There are 1 figure, 2 tables, and 9 references, 4 of which are Soviet.

PRESENTED: March 4, 1959, by B. A. Arbuzov, Academician

SUBMITTED: February 28, 1959

Card 3/3

5(4) SOV/20-127-2-[illegible]/70

AUTHORS: Polyakova, A. A., Zimina, K. I., Petrov, A. A.,
Khmel'nitskiy, R. A.

TITLE: Mass Spectra and Structure of Vinyl Acetylene Hydrocarbons

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 2, pp 386-389
(USSR)

ABSTRACT: Investigations of relations existing between physical properties influencing structure and reactivity supply data for infrared spectra (Ref 2), Raman spectra (Ref 3), and dipole moments (Ref 4). Results obtained from investigations with the MS-1 mass spectrograph are reported here. The mass spectra of vinyl acetyl and of its three monomethyl derivatives were taken. Results are specified in table 1. Maximum intensity is exhibited by the molecular ion. The most intense split ions are produced by the rupture of the C-H bond. Split ions produced by the rupture of the C-C bond are not typical of these compounds. Unlike piperylene and isoprene, the introduction of a methyl radical decreases but little the stability of the molecular ion. The normal chain isomers differ from isopropyl acetylene by a greater intensity of the peak 63 ($C_5H_3^+$-Ion).

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Mass Spectra and Structure of Vinyl Acetylene Hydrocarbons SOV/20-127-2-42/70

A striking fact is that the greatest stability is exhibited by those split ions which have conjugate bonds. It would be interesting to compare these properties with data concerning the kinetics of the ion reactions of vinyl acetylenes. Unfortunately, there are no such data available in publications. There are 1 table and 6 references, 5 of which are Soviet.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut po pererabotke nefti i gaza i polucheniyu iskusstvennogo zhidkogo topliva (All-Union Scientific Research Institute for Petroleum and Gas Refining and Production of Synthetic Liquid Fuels)

PRESENTED: March 26, 1959, by B. A. Arbuzov, Academician

SUBMITTED: March 21, 1959

Card 2/2

5.3700(B)

[illegible]6[illegible]

S/153/60/003/01/0[illegible]
B011/B005

AUTHORS: Petrov, A. A., Kormer, V. A.

TITLE: On the Addition of Lithium Alkyls on Divinyl Acetylene

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1960, Vol 3, Nr 1, pp 112-114 (USSR)

TEXT: The authors' experiments showed that lithium alkyls readily react with
divinyl acetylene. Industrial divinyl acetylene with small impurities of
acetylenyl divinyl and about 20% of xylene, lithium ethyl, 2 isomeric lithium
butyls, and lithium amyl were used for this purpose. With each of the lithium
alkyls mentioned, divinyl acetylene could form 6 different adducts (1,2-, 1,4
and 1,6-addition) with triene- or enine groups. The authors, however, expected
that only vinyl-allene hydrocarbons would form on the basis of the rules
established before: $CH_2=CH-CH=C=CH-CH_2-R$ (after treating the adducts
with water). The acetylenyl divinyl present as an admixture would not take an
active part in the formation of monomer products. The experiments confirmed this
assumption. Only 1,3,4-triene hydrocarbons were formed. They contained only
traces of acetylene compounds. The structure of the reaction products was proved
on the basis of their infrared and ultraviolet spectra as well as by hydro-
genation to saturated hydrocarbons. A normal structure of the hydrocarbons used

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69673

On the Addition of Lithium Alkyls on Divinyl Acetylene

S/153/60/003/01/029/058
B011/B005

was proved in all cases. There were no fully conjugate trienes. Table 1 presents the constants of the vinyl allenes obtained for the first time. Vinyl allenes have much smaller refractive indices than 1,3,5-trienes. The figure (p 114) shows the infrared spectra of trienes recorded by an IKS-14 spectrophotometer. The spectra will be described and analyzed in a separate paper. There are 1 figure 2 tables, and 5 references, 4 of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut im. Lensoveta; Kafedra organicheskoy khimii (Leningrad Technological Institute imeni Lensovet; Chair of Organic Chemistry)

SUBMITTED: April 13, 1959

Card 2/2

83507

S/074/60/029/009/001/002
B013/B064

5 3300 also 2109, 2209

AUTHOR: Petrov, A. A.

TITLE: Vinyl Acetylene and Its Homologs

PERIODICAL: Uspekhi khimii, 1960, Vol. 29, No. 9, pp. 1049-1106

TEXT: The present survey deals with the methods of synthesizing enin hydrocarbons and their properties. Before the Thirties, these compounds had been investigated only little (Refs. 1-16). The majority of known enin hydrocarbons have been described in the course of the last twenty years. Table 2 shows their formulas and constants. Enin hydrocarbons can be synthesized by various methods; the most frequently used starting material is acetylene. Enin hydrocarbons can be 1) synthesized from compounds with the same number of hydrocarbon atoms. The following methods of preparation are described in this connection: synthesis from halogen derivatives (Refs. 2, 7, 8, 20-48), dehydration of acetylene alcohols (Refs. 10, 14, 49-109), separation of alkyl hypohalogenites of acetylene-β ether halides (Refs. 110, 114), total methylation of unsaturated amines (Refs. 4-9, 115-119), and selective hydrogenation of diacetylenes (Refs.

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Vinyl Acetylene and Its Homologs

S/074/60/029/004/001/002
B013/B064

[illegible]). It is also possible to synthesize enin hydrocarbons from compounds with a smaller number of carbon atoms. In this case the following methods are applied: dimerization of acetylene hydrocarbons (Refs. [illegible]), reactions of metal acetylides with halogen derivatives (Refs. [illegible] 174), reactions of propargyl halides with unsaturated organo-metallic compounds (Refs. 169, 175, 176), alkylation of vinyl acetylene [illegible] molecules having an acetylene end group (Refs. [illegible]) and the [illegible] synthesis of enin hydrocarbons from compounds with a greater number of carbon atoms (decomposition of acetylene [illegible]) is treated in Refs. 183-186. The physical properties of enin hydrocarbons (Tables [illegible]) are described in Refs. 7, 18, [illegible] 20, [illegible] 244. The chemical properties of enin hydrocarbons [illegible] depend on the presence of multiple bonds, especially on a conjugated [illegible] acetylene system [illegible] the hydrogen atom bound to the acetylene [illegible]. The following reactions belong to the first group of conversions: addition, formation of complex compounds, homo- and heterocyclization as well as polymerization. The second group of reactions comprises [illegible] of hydrogen by halogens, metals, and other elements, as [illegible] condensation with carbonyl compounds. The following reactions [illegible]

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Vinyl Acetylene and Its Homologs

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B013/B064

multiple bonds are described: the effect of oxidizing agents (Refs. 4, 77, 78, 99, 198, 245-255), hydrogenation (Refs. 28, 52, 72, 220, [illegible]), addition of halogens (Refs. 2, 28, 29, 52, 43, 4[illegible], 46, 166, [illegible]-286), addition of hydrogen halides (Refs. 71, 74, 166, 178, 287-301), addition of hypohalogen acids and their esters (Refs. 166, 302-309), addition of water, alcohols, acids, and phenols (Refs. 56, 121, 310-[illegible]), addition of sulfur-, nitrogen-, phosphorus-, and silicon compounds (Refs. [illegible]), addition with lengthening carbon chain. This group comprises reactions with: acetylenes (Ref. 368), free radicals (Ref. 369), organic lithium compounds (Refs. 370-372), halogen derivatives (Refs. [illegible]), hydrogen cyanide (Ref. 378), nickel carbonyl (Refs. 379-382), dialkyl carbonates (Ref. 383), and diazo compounds (Refs. 384-388). Some cases of isomerization with a shift of the multiple bonds are described (Refs. 20, 22, [illegible], 180, 389, 390). Refs. 1, 8, 74, 141, 188, 356, 391-416 deal with the dimerization and polymerization of vinyl acetylene and its homologs, Ref. 417 with the addition of fluoroolefines, and Refs. 418-423 with the formation of complex compounds. Refs. 424-430 describe the substitution of acetylene hydrogen by halogens and Refs. 2, 9, 11, 12, 100, [illegible], 431-43[illegible] substitution by metals and metalloids. Condensation with carbonyl compounds

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Vinyl Acetylene and Its Homologs

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B014/B064

at the expense of acetylene hydrogen is described in Refs. [illegible] [illegible] 41 [illegible] and [illegible] ve [illegible] in Refs. [illegible] and [illegible] [illegible]rskiy, Reformatskiy, A. L. Klebanskiy, N. I. Zelinskiy, S. V. Lebedev, I. V. Sarmanov, K. K. Chevychalova, Kucherov, Markovnikov, Ya. M. [illegible], A. V. Dombrovskiy, S. A. Vartanyan, and I. N. Nazarov are mentioned. There are 4 tables and 476 references, [illegible] Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut im. [illegible] (Leningrad Technological Institute imeni [illegible])

Card 4/4

[illegible]

AUTHORS: [illegible]

TITLE: [illegible]

PERIODICAL: [illegible]

ABSTRACT: [illegible]

Card [illegible]

[illegible]

[illegible]

ASSOCIATION: [illegible]

SUBMITTED: [illegible]

Card [illegible]

Card 4

Table [illegible]

[illegible]

[illegible]		petroleum ether
		ethyl ether
	[illegible]	petroleum ether
	[illegible]	ethyl ether
	[illegible]	ethyl ether
[illegible]		petroleum ether
	[illegible]	ethyl ether
	[illegible]	ethyl ether
	[illegible]	ethyl ether
	[illegible]	petroleum ether
		ethyl ether

Card [illegible]

AUTHORS: [illegible]

TITLE: [illegible]

PERIODICAL: [illegible]

ABSTRACT: [illegible]

AUTHORS: [illegible]

TITLE: [illegible]

PERIODICAL: [illegible]

ABSTRACT: [illegible]

S/079/60/030/04/[illegible]
B001/B016

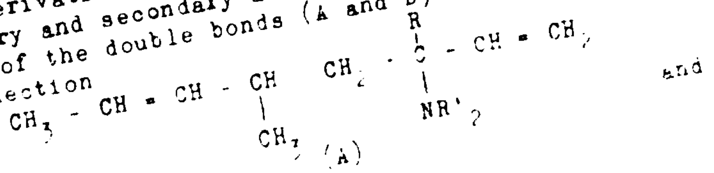
5 3610

AUTHORS: Petrov, A. A., Razumova, N. A., Genusov, M. L., Yakovleva, [illegible]

TITLE: Exchange Reactions of Telomers of Diene Hydrocarbons Containing Chlorine. I. Reactions Between Some Low Telomers of Diene Hydrocarbons and Amines

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 4, pp [illegible]

TEXT: In continuation of the papers by the authors of the present [illegible] (Ref. 1) and the papers of Ref. 2, it was of interest to allow [illegible] of 2-chloro pentene-3 to dienes which may also be regarded as al[illegible] halogen derivatives to react with nucleophilic reagents, [illegible] the primary and secondary amines. Two types of compounds with [illegible] position of the double bonds (A and B) may be expected to be form[illegible] this connection



$CH_3-CH=CH-\underset{\displaystyle CH_3}{CH}$ (A)

$CH_2-\overset{\displaystyle R}{\underset{\displaystyle NR'_2}{C}}-CH=CH_2$ and

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5 3600

S/079/60/030/04/23/080
B001/B016

AUTHORS: Petrov, A. A., Bunina-Krivorukova, L. I.

TITLE: Exchange Reactions of Telomers of Diene Hydrocarbons Containing Chlorine. II. Reaction of 1-Chloro-5-methyl-, 1-Chloro-3,5-dimethyl-, and 1,3-Dichloro-5-methyl octadiene-2,6 With Sodium Acetoacetic Ester

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, No 4, pp 1165-1168

TEXT: In continuation of their previous paper (Ref. 1), the authors described in the present one the above-mentioned exchange reactions which are of interest as intermediate stages in the synthesis of alcohols of the sesquiterpene series, their homologs and analogs. From among the numerous reactions of allyl halogen derivatives with sodium acetoacetic ester described in publications those are important for the present investigation in which crotyl chloride, prenyl chloride, and 1,3-dichloro butene 2 take part since these chlorides contain the same atom grouping in end position as the telomers investigated previously by the authors. All chlorides mentioned yielded ketones as end products which contain no

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Exchange Reactions of Telomers of Diene Hydrocarbons Containing Chlorine. II. Reaction of 1-Chloro-5-methyl-, 1-Chloro-3,5-dimethyl-, and 1,3-Dichloro-5-methyl octadiene-2,6 With Sodium Acetoacetic Ester

S/079/60/030/04/23/080
B001/B016

vinyl group (Refs. 2-7) 2-Methyl hepten-2-one-6 was obtained, in this special case, from prenyl chloride (Refs 2,5) The reactions of 1-chloro-5-methyl-, 1-chloro-3,5-dimethyl-, and 1,3-dichloro-5-methyl octadiene-2,6 (telomers of 2-chloro pentene-3 with divinyl isoprene and chloroprene) with sodium acetoacetic ester showed in the infrared spectra investigated (Diagram) that also in this case ketones without vinyl groups occur as end products (Table 1). Thus, isomeric ketones of the type $CH_2=CH-CR_2-CH_2-CO-CH_3$, which should be present in the case of a [illegible] allyl rearrangement, could not be detected. The resultant ketones are colorless oils with peculiar, pleasant odor Three ketones, 4-methyl-undecadiene-2,6-one-10, 4,6-dimethyl-undecadiene-2,6-one-10, and 6-chloro-4-methyl-undecadiene-2,6-one-10 were described There are 1 figure, 2 tables, and 8 references, 6 of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Institute of Technology imeni Lensovet)

Card 2/3

5.3200

S/079/60/030/05/09/074
B005/B002

AUTHORS: Petrov, A. A., Porfir'yeva, Yu. I., Yakovleva, T. V.

TITLE: Investigations in the Field of Conjugate Systems. CXVII. On the Problem of the Direction of the Addition of Halogens to Vinyl Acetylene Hydrocarbons

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 5, pp. 1441-1444

TEXT: The authors of the present paper describe their investigations concerning the addition of chlorine and iodine bromide to vinyl acetylene and vinyl ethyl acetylene. Iodine bromide lies between bromine and iodine as to its reactivity and has a dipole moment of 0.4 Debye (Ref. 5). The structures of the addition products were determined by analyzing their infrared spectra. On the addition of chlorine to vinyl acetylene there occurs a mixture of allene- and acetylene derivative with a low percentage of dichloride of butadiene. Chlorine therefore behaves in much the same way as bromine in the reaction with vinyl acetylene, the only difference being in that a larger amount of 3,4-addition product and a smaller amount of 1,2-addition product are obtained on a chlorine addition

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Investigations in the Field of Conjugate Systems CXVII. On the Problem of the Direction of the Addition of Halogens to Vinyl Acetylene Hydrocarbons

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than would be the case with bromine addition. The main product to result on the chlorination of vinyl ethyl acetylene is the acetylene derivative with a very small admixture of 1,3-diene derivative. Thus, chlorine behaves here in much the same way as bromine. Unlike chlorine, iodine bromide is preferably added to the triple bond in both hydrocarbons under investigation. Addition to the double bond occurs to a small extent, while the corresponding allene derivatives are formed in an inconsiderable amount. Therefore, iodine bromide behaves in much the same way as iodine on the addition. The procedures followed in the investigations are described in an experimental part. Yields, boiling points, densities, and refractive indices of the dihalide mixtures obtained are specified along with the elementary per cent analyses. The characteristic frequencies of the infrared spectra of the mixtures obtained are specified as well. In all cases, the dihalides were isolated by the vacuum distillation of the reaction products, since large amounts of high-boiling higher halides were also obtained on halogenization. To eliminate the possibility of an error due to an isomerization of the reaction

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Investigations in the Field of Conjugate Systems. CXVII. On the Problem of the Direction of the Addition of Halogens to Vinyl Acetylene Hydrocarbons

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B005/B002

products during distillation, the infrared spectra of the crude reaction products were investigated as well. In all cases, these spectra contained the characteristic bands of such dihalides as were afterwards isolated from the mixtures. A figure shows the infrared spectra of the 4 mixtures of dihalogen hydrocarbons obtained. There are 1 figure and 7 Soviet references.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Institute of Technology imeni Lensovet)

SUBMITTED: April 22, 1959

S/079/60/030/05/10/074
B005/B002

5,3200

AUTHORS: Chelpanova, L. F., Nemirovskiy, V. D., Petrov, A. A., Yakovleva, T. V.

TITLE: Investigations in the Field of Conjugate Systems. CXVIII. On the Direction of the Addition of Bromine to Vinyl Acetylene Ketones

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 5, pp. 1445-1450

TEXT: By way of introduction the authors offer a brief survey of publications concerning the rules governing the addition of bromine to vinyl acetylene hydrocarbons (Refs. 1-4) and to derivatives of vinyl acetylene hydrocarbons (Refs. 5, 6). In the paper under review, they describe the results of their investigations on the direction of bromine addition to vinyl acetylene ketones of the following two types (I) and (II):

$CH_3-CO-CH=CH-C\equiv CH$ (I)

$R-CO-C\equiv C-CH=CH_2$ (II)

(IIa) $R = CH_3$; (IIb) $R = C_2H_5$;

(IIc) $R = n-C_3H_7$

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Investigations in the Field of Conjugate Systems. CXVIII. On the Direction of the Addition of Bromine to Vinyl Acetylene Ketones

S/079/60/030/05/10/074
B005/B002

The structures of the addition products were defined by the analysis of their infrared spectra Spectroscopic measurements were made on a spectrophotometer of type ИКС-14 (IKS-14). The characteristic frequencies of the two compound types (I) and (II) are given. To determine the direction of the bromine addition to the ketones mentioned, the infrared spectra of the solutions of these ketones in carbon tetrachloride were compared with the spectra of solutions of bromination products in the same solvent. Since the bromides were not isolated from the reaction mixtures, the results supplied refer to the original products of bromination. On the bromination of ketone (I) with the equimolar amount of bromine, this is preferably added to the triple bond At the same time there also occurs an addition to the double bond, giving rise to a non-conjugate system The 1,4-addition which is characteristic of the respective hydrocarbon, does not occur in the case of the ketone On the bromination of ketones (IIa), (IIb), and (IIc), the addition to the triple bond and the addition to the double bond proceed together A [illegible] does not occur here either. The dibromides of ketone (I) could not be isolated, since a decomposition took place on distillation of the

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Investigations in the Field of Conjugate Systems. CXVIII. On the Direction of the Addition of Bromine to Vinyl Acetylene Ketones

S/079/60/030/05/13/074
B005/B002

reaction mixture The dibromides of ketone (IIa) were isolated from the reaction mixture. The analysis of their infrared spectrum, shown in Fig. 4, confirmed the above statement concerning the direction of bromine addition. It may be stated in conclusion that vinyl acetylene ketones add bromine to a considerably less selective extent than the respective hydrocarbons Another characteristic feature is the complete absence of 1,4-addition, as well as the relatively high reaction rate of bromine addition The otherwise low reactivity of the triple bond is increased by the carbonyl group It proceeds therefrom that the addition of bromine to the ketones mentioned is probably a nucleophilic reaction (cf also Refs 9-11) An experimental part contains data on production, along with main physical data and the characteristic infrared frequencies of the 4 ketones investigated The reaction conditions in bromination and the physical data of the isolated mixture of the dibromides of the ketone (IIa) are specified as well Figs 2 and 3 show the infrared spectra of the 4 ketones investigated and the products of their bromination There are 4 figures and 15 references: 9 Soviet, 2 English, and 2 German

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Investigations in the Field of Conjugate Systems. CXVIII. On the Direction of the Addition of Bromine to Vinyl Acetylene Ketones

S/079/60/030/05/10/074
B005/B002

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Institute of Technology imeni Lensovet)

SUBMITTED: May 25, 1959

Card 4/4

5.3200

S/079/60/030/05/11/074
B005/B002

AUTHORS: Petrov, A. A., Kolyaskina, Z. N.

TITLE: Reactions of Chlorine-containing Telomers of Diene Hydrocarbons. III. Production of Aldehydes and Ketones From the Products of the Addition of Tertiary Butyl Chloride to Divinyl and Chloroprene

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 5, pp. 1450-1454

TEXT: The investigation of the telomerization reaction of diene hydrocarbons with saturated alkyl halides showed that only tertiary alkyl halides secure good yields of monomeric addition compounds of the type $R-C_4H_6-Cl$ (Ref. 1). The authors of the present paper investigated the conversion of these halogen-containing addition products in unsaturated aldehydes and ketones with a quaternary carbon atom. The scheme of this reaction is given. On the addition of tertiary butyl chloride to butadiene there arises 1-chloro-5,5-dimethyl-hexene-2. The structure of this product was clearly defined by analyzing its infrared spectrum (Fig. 1).

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Reactions of Chlorine-containing Telomers of Diene Hydrocarbons. III Production of Aldehydes and Ketones From the Products of the Addition of Tertiary Butyl Chloride to Divinyl and Chloroprene

S/079/60/030/05/11/074
B005/B002

The product of the addition of tertiary butyl chloride to chloroprene had already been obtained at the authors' laboratory in 1953, but the data concerning this compound had not been published. The analysis of the infrared spectrum (Fig. 1) showed that this product is 1,3-dichloro-5,5-dimethyl hexene-2. The two unsaturated chlorides mentioned were converted into the corresponding unsaturated aldehydes by the aid of Sommle's reaction (Ref. 3). In this manner, 5,5-dimethyl hexene-2-al (I) was obtained from 1-chloro-5,5-dimethyl-hexene-2, and 3-chloro-5,5-dimethyl hexene-2-al (II) was obtained from 1,3-dichloro-5,5-dimethyl hexene-2. Both aldehydes were obtained in the form of colorless oils with a hay-like smell, which turned into yellow on a longer standing time. Aldehydes are insoluble in water, but are readily soluble in the usual organic solvents. Fig. 2 shows the infrared spectra of the two aldehydes Data obtained from the interpretation of spectra are given. Both aldehydes readily form semicarbazones and 2,4-dinitrophenyl hydrazones, which are well crystallizable. On the condensation of the mentioned aldehydes with

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Reactions of Chlorine-containing Telomers of Diene Hydrocarbons III. Production of Aldehydes and Ketones From the Products of the Addition of Tertiary Butyl Chloride to Divinyl and Chloroprene

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B005/B002

acetone in the presence of sodium alcoholate, diene ketones were obtained in the form of pale-yellow oils with a pleasant smell. The infrared spectra of the two ketones (2,2-dimethyl nonadiene-4,6-one(8), and 4-chloro-2,2-dimethyl nonadiene-4,6-one(8)) respectively, are likewise shown in Fig. 2. On the hydrogenation of aldehyde (I) in the presence of colloidal palladium, the main resulting product is 5,5-dimethyl hexanal, which, however, contains an admixture of the corresponding alcohol. Hence, hydrogenation does not proceed selectively under these conditions. Investigations revealed that the telomerization reaction can be applied to the production of a number of unsaturated aldehydes and ketones with a quaternary carbon atom from diene compounds. All the operations are described in great detail in the experimental part of the paper. Yield, boiling point, refractive index, density, and characteristic frequencies of the infrared spectrum are specified for each of the products obtained. The infrared spectra were taken by means of a spectrophotometer of type ИКС-14 (IKS-14),[24] and an apparatus of type ИКС-2 (IKS-2)[24] was used in one

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Reactions of Chlorine-containing Telomers of Diene Hydrocarbons. III. Production of Aldehydes and Ketones From the Products of the Addition of Tertiary Butyl Chloride to Divinyl and Chloroprene

S/079/60/030/05/11/074
B005/B002

case. There are 2 figures and 4 Soviet references.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Institute of Technology imeni Lensovet)

SUBMITTED: May 25, 1959

Card 4/4

85389

S/079/60/030/006/016/033/XX
B001/B055

5-3600

AUTHORS: Petrov, A. A. and Porfir'yeva, Yu. I.

TITLE: Investigations in the Field of Conjugated Systems. CXIX. The Mode of Electrophilic Addition in Unsymmetrical Dienes. The Effect of Benzene-sulfone-dibromoamide on Alcoholic Solutions of Divinyl-acetylene and Its Homologs

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, No 6, pp 1816-1821

TEXT: Basing on Refs 1-4, the authors studied the reaction of three hydrocarbons of the series C_nH_{2n-6} (hexadien-1,5-yne-3, 2-methyl-hexadien-1,5-yne-3, 3-methyl-heptadien-2,6-yne-4) with benzene-sulfone-dibromoamide in methanol in order to determine how the direction of polarization in unsymmetrical diene molecules affects the order of addition of electrophilic reagents. The bromine atom fixed the point of initial electrophilic attack, i.e., the point of highest electron density at the moment of reaction (Refs 5, 6). Since the authors found (Ref 7) that in vinyl-acetylene hydrocarbons hypobromites are predominantly added to the

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85389

Investigation in the Field of Conjugated S/079/60/030/[illegible] XX
Systems. CXIX. Mode of Electrophilic Addition to B001/B0[illegible]
Unsymmetrical Dienes. The Effect of Benzene-
sulfone dibromoamide on Alcoholic Solutions of
Divinyl acetylene and Its Homologs

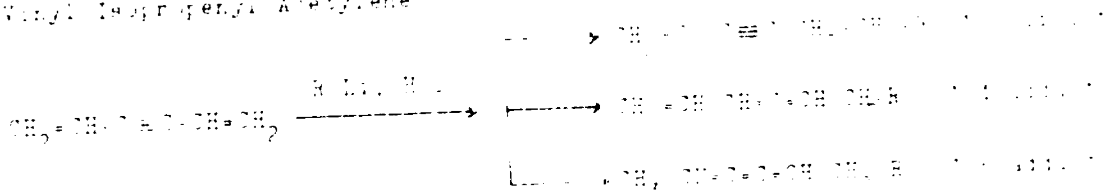
[illegible] ned hydrocarbons [illegible] the substituted vinyl group. The point of electrophilic addition in the diene system was found to correspond to the electron configuration. The constants of the vinyl acetylene bromo ethers are given in Table [illegible] and all known β alkoxy divinyl acetylenes are characterized more closely in Table [illegible]. There are [illegible] figure, [illegible] tables, and [illegible] Soviet references.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta
(Leningrad Institute of Technology imeni Lensovet)

SUBMITTED: June [illegible]

Card [illegible]

Investigations in the Field of Conjugate [illegible]
Systems CXX Addition of Lithium Alkyls [illegible]
Vinyl Isopropenyl Acetylene



It has already been shown that the addition of lithium alkyls to [illegible] acetylene takes place in the 1,4-position to give vinyl allene [illegible] (Ref 1). The structures of the latter were confirmed by their infrared spectra (absorption bands of the vinyl group and of the allene system without those of the acetylene group) and by exhaustive hydrogenation. In the present paper the addition of lithium to vinyl isopropenyl [illegible] was studied. Due to its unsymmetrical structure, the addition may take place in this case to the vinyl or isopropenyl group [illegible] of Ref [illegible] (I) and (II). On the strength of the [illegible] addition of radicals to the vinyl group had to be expected [illegible] had lost electrons. The same mode of addition was predicted [illegible] radical character of the reaction course, since radical processes are

Card 2/3

85611

5 3600 2209, 1153

[illegible]

AUTHORS: Petrov, A. A., Kormer, V. A., and Stadnichuk, M. D.

TITLE: Investigations in the Field of Conjugate Systems. [illegible] Addition of Lithium Alkyls to Trialkylvinyl Acetylenyl Silane

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. [illegible], pp. [illegible]

TEXT: The authors continued their investigation of the reaction of lithium alkyls with compounds having a double and a triple bond, and studied, taking into account the papers of Refs. 3, 4, the addition of lithium ethyl, propyl, isopropyl, butyl, and tertiary butyl to trimethylvinyl acetylenyl silane. By treating the reaction product with water they obtained the addition products of the expected composition. $(CH_3)_3Si$ [illegible] ing to the mode of addition of lithium alkyls, structures I to VI were possible. In the infrared spectra of all adducts, frequencies of the stretching vibrations of a triple and allene bond system were found. In the spectral region which is characteristic of the stretching vibrations of the double bond [illegible] Diagram [illegible]

Card 1/3

[illegible]

Investigations in the Field of Conjugate Systems CXXI Addition of Lithium Alkyls to Trialkylvinyl Acetylenyl Silane

S/079/60/[illegible]/XX
B001/B06[illegible]

data show that the adducts are mixtures of acetylene and allene compounds and that formulas (IV) and (V) are negligible. On hydrogenation of the silicon hydrocarbons obtained from the adducts with lithium methyl and lithium butyl by means of Pd/CaCO$_3$, trimethylhexyl and trimethyloctyl silane were obtained accordingly. Their structure was confirmed by comparing their infrared spectra with those of authentic samples of silicon hydrocarbons (Diagram 2). Thus all formulas except (I) and (II) may be excluded. The ratio between the acetylene and allene isomers was found from their hydrolysis. The hydrolytic cleavage of two silicon hydrocarbons with R = C_2H_5 and C_4H_9 gave hexamethyldisiloxane and mixtures of acetylene-allene hydrocarbons, C_6H_{10} and C_8H_{14}, according to the scheme:

$$(I) \longrightarrow HC\equiv C-CH_2-CH_2-R + (CH_3)_3Si-O-Si(CH_3)_3$$

$$(II) \longrightarrow CH_2=C=CH-CH_2-R + (CH_3)_3Si-O-Si(CH_3)_3$$

Since hydrolysis took place at [illegible] 70° allene-acetylene isomerization was impossible in this case. The acetylene isomer content in the mixture was determined analytically (Ref. [illegible]). Also the difference between the

Card 2/3

Investigations in the Field of Conjugated [illegible]
Systems. CXXI. Addition of Lithium [illegible]
to Trialkylvinyl Acetylenyl Silane

molecular refraction of (I) and (II) permits to estimate the relative composition of the adduct mixtures of (I) and (II). It was thus shown that lithium alkyls add to trimethylvinyl acetylenyl silane and give a mixture of acetylene and allene compounds. They add in another way as the vinyl alkyl acetylenes. The course of the curve (Diagram 4) showing the hydrogenation rate of the mixtures of adducts (I) and (II) is remarkable. The authors mention A. D. Petrov, G. I. Saidykhanidze, and V. F. Yegorov. They express their gratitude to T. V. Yakovleva for examining the infrared spectra. There are 4 figures, 1 table, and 7 references, 6 Soviet and 1 US.

ASSOCIATION Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Technological Institute imeni Lensovet)

SUBMITTED July [illegible], 1959

Card [illegible]

5 3400 2209 [illegible]

[illegible]

AUTHORS: Petrov, A. A., [illegible], K. S., Maretina, I. A., Nemirovskiy, V. D.

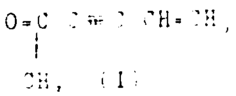
TITLE: Investigations in the Field of Conjugated Systems. CXXII. Dipole Moments and Reactivity of Vinyl Acetylene Ketones and Amines

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7, pp. 2148-[illegible]

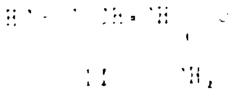
TEXT: Following their papers (Refs. 1-4) on the interpretation of rules governing the reactivity of vinyl acetylene hydrocarbons the authors determined the dipole moments of two vinyl acetylene ketones (I) and (II) of different structures and of amine (III). The dipole moment of ketone (I) was found to be much larger than the moments of methyl vinyl ketone (Ref. 5) and mesityl oxide (Ref. 6). The dipole moment of ketone (II) [illegible] moments of the carbonyl group and of the enine system opposite to each other was lower than in the case of methyl vinyl ketone. The same ratio also existed between the polarizability of these ketones (Table 1)

Card 1/3

Investigations in the Field of Conjugated S[illegible]
Systems. CXXII. Dipole Moments and React[illegible]
of Vinyl Acetylene Ketones and Amines


(I)

$\underset{\mathrm{CH_3}}{\mathrm{O{=}C}}\mathrm{{-}C{\equiv}C{-}CH{=}CH_2}$


(II)

Vinyl acetylene amine (III), in the molecule of which a conjugation exists between the electron pair of the nitrogen atom and the enin system, showed a very large dipole moment, whereas saturated and unsaturated amines without such a structure have small moments (Refs 7 - 9).

$\mathrm{HC{\equiv}C{-}CH{=}CH{-}N(C_2H_5)_2}$ (III). This agreement between the magnitude [illegible] expected for the dipole moment under the conjugation effect and those observed in experiments support the earlier assumption of the electron displacement in the enin systems. Vinyl acetylene amine (III) adds on [illegible] primarily to the triple bond. This corresponds to that electron [illegible] which might be assumed from the magnitude of the dipole moment (Ref. 12). Consequently a certain dependence exists in these cases between polarity in the steady state and the reactivity of the derivatives of vinyl acetylene hydrocarbons. There are 2 tables and [illegible] references, [illegible] Soviet, [illegible] US, and [illegible] British.

Card [illegible]/3

Investigations in the Field of Conjugated [illegible]
Systems. CXXII. Dipole Moments and [illegible] [illegible]
of Vinyl Acetylene Ketones and Amine [illegible]

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta
(Leningrad Technological Institute imeni Lensovet)

SUBMITTED July [illegible]

Card 3/[illegible]

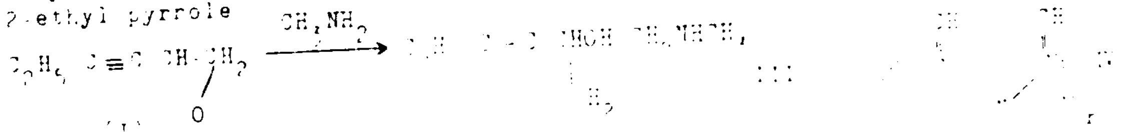
[illegible]
[illegible]1, B06[illegible]

AUTHORS: Al'bitskaya, V. M., [illegible], Ye. M., and Petrov, [illegible]

TITLE: Investigations in the Field of Chemistry of [illegible] Oxides. XVII. Reaction of Primary secondary Acetylene Oxides With Methyl Amine

PERIODICAL: Zhurnal obshchey khimii, [illegible], Vol. [illegible], No. [illegible]

TEXT: Taking into account the papers of Refs. [illegible] on the fundamental laws of the reactions of saturated α oxides with amines and ammonia, the authors reacted the two acetylene oxides 1,2-epoxy hexine-3 (I) and 1,2-epoxy octine-3 (II) with methyl amine. Oxide (I) reacted with methyl amine to give a mixture of amino alcohol (III) and N methyl 2-ethyl pyrrole (IV). When [illegible] dehydrated with potassium hydroxide the amino alcohol (III) gave N methyl-2-ethyl pyrrole



(I)

Card 1/2

Investigations in the Field of Chemistry of Organic Oxides. XVII. Reaction of Primary-secondary Acetylene Oxides With Methyl Amine

S/079/[illegible]
[illegible]

Reaction of oxide (II) with methyl amine gave only N-methyl- [illegible] pyrrole (V). The formation of substituted pyrroles indicates that the [illegible] of the amine to the oxide ring takes [illegible] the rule of Krasuskiy. The samples of pyrroles (IV) and (V) are [illegible] of a characteristic odor which [illegible] moistened with hydrochloric acid red. With SeO_2 they turn violet. They form mercury derivatives and azo compounds. The infrared spectra of both products show absorption bands characteristic of pyrroles (Ref. [illegible]). The experiments performed show that primary-secondary acetylene oxides reacting with amines behave like primary and secondary-tertiary acetylene oxides. F. Ya. Perveyev is mentioned. There are [illegible] references: [illegible] Soviet and [illegible]

ASSOCIATION Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Technological Institute imeni Lensovet)

SUBMITTED July [illegible]

Card [illegible]/2

S[illegible] XX
[illegible]

AUTHORS Petrov, A. A. and K[illegible]

TITLE Mode of Addition of Water and Alcohols to Vinyl Acetylene Hydrocarbons

PERIODICAL Zhurnal obshchey khimii [illegible]

TEXT The addition of water under the conditions of Kucherov's reaction [illegible] is analogous to that of alcohols in the presence of KOH to vinyl alkyl acetylenes and corresponds to the theory of electron displacements (Ref. [illegible]). But to isopropenyl alkyl and vinyl isopropenyl acetylenes water does not add according to polarization, as might be expected for these hydrocarbons. This anomalous mode of addition may be explained by steric hindrances in the intermediate formation of a mercury complex under the conditions of Kucherov's reaction, assuming that the reaction has an electrophilic character in the first stage: a radical on C_1 hinders the access of mercury to C_2. To confirm this assumption it had to be shown that the [illegible] addition of nucleophilic reagents such as methyl alcohol in the presence [illegible]

Card 1/2

Mode of Addition of Water and Al[illegible] [illegible]
Vinyl Acetylene Hydr[illegible]

[illegible]

of KOH, takes place without catalysts [illegible] general rule. The addition of methyl alcohol to isopropenyl methyl acetylene in the presence of KOH gave an enol ether boiling at [illegible] and on hydrolytic cleavage with dilute sulfuric acid yielded mesityl oxide which contained no ethyl isopropenyl ketone impurity. On hydrogenation with Pd $CaCO_3$ catalyst, mesityl oxide gave methyl isobutyl ketone, which according to the constants, the infrared spectrum, and the melting point of the 2,4-dinitrophenyl hydrazone, was identical with a methyl isobutyl ketone sample of known composition. It was found that the mode of nucleophilic addition of alcohol to isopropenyl methyl acetylene differs from that of water under the conditions of Kucherov's reaction. This confirms the previous assumption regarding the mechanism of this reaction and the causes of anomalous addition of water. There are [illegible] Soviet references.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Technological Institute imeni Lensovet)

SUBMITTED: March [illegible]

Card 2/2

AL'BITSKAYA, V.M.; BLYAKHMAN, Ye.M.; PETROV, A.A.

Chemistry of organic oxides. Part 18: Order of addition of alcohols to chloroprene oxide in the presence of alcoholates and boron fluoride etherate. Zhur.ob.khim. 30 no.8:2524-2527 Ag '60. (MIRA 13:8)

1. Leningradskiy tekhnologicheskiy institut imeni Lensoveta.
(Alcohols) (Butadiene)

5 3600 2209.1153

[illegible]

[illegible]

S/079/60/030/[illegible]
B00[illegible]/B06[illegible]

AUTHORS: Polyakova, A. A., [illegible], Petrov, A. A., and
Khmel'nitskiy, R. A.

TITLE: Mass Spectra and Structure of Some Allene Hydrocarbons

PERIODICAL: Zhurnal [illegible] khimii, [illegible], Vol. [illegible], No. [illegible],
pp. [illegible] - [illegible]

TEXT: Following the articles of Refs. [illegible] on the interaction of molecules of unsaturated compounds with electrons and on the correlation between their structure and their mass spectra, the authors investigated the mass spectra of some allenes (1,2- and 2,3-dienes) on a MC-1 (MS-1) mass spectrograph in order to determine the effect of the position of the double bonds upon the main formation of these or those ions in the electron collision, as well as to compare these data with the characteristic mass spectra of other hydrocarbons. Ions formed by cleavage of the [illegible]

Card 1/[illegible]

Mass Spectra and Structure [illegible] [illegible]
Al[illegible]ne Hydrocarb[illegible]

predominate in the mass spectra [illegible] The [illegible] concentration of the C – [illegible] for the ions $C_3H_x^+$ and $C_4H_x^+$ [illegible] in alkanes, like [illegible] the [illegible] mentioned, the mass spectra of [illegible] which [illegible] (4 dienes) are characterized [illegible] dent on the structure. The [illegible] described [illegible] cation [illegible] In the spectra of [illegible] maximum [illegible] the peak 67 of the mass shows the maximum [illegible] of the mass. In the [illegible] spectra of the 2,7-dienes, the peak [illegible] $C_3H_x^+$ [illegible] 2,7-dimethyl octadiene, the peak [illegible] maximum intensity. The second maximum [illegible] the ions $C_3H_x^+$. An attempt [illegible] to explain the [illegible] the formation [illegible] intense ions with respect [illegible]

Card [illegible]

Mass Spectra and Structure of [illegible] Allene Hydrocarbons

[illegible]/60/0[illegible]0/00[illegible]/0[illegible] [illegible] /X7
[illegible]/B0[illegible]

mechanism assumed for the splitting [illegible] the [illegible] potentials were investigated. Sensitivity and complete [illegible] of all allenes studied were determined, and the degree of [illegible] was found to be dependent on the hydrocarbon structure. There are 3 figures, 2 tables, and [illegible] references: [illegible] Soviet [illegible]

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut po pererabotke nefti i gaza; Leningradskiy tekhnologicheskiy institut imeni Lensoveta
(All-Union Scientific Research Institute for the Processing of Oil and Gas; Leningrad Technological Institute imeni Lensoveta)

SUBMITTED: September [illegible]

Card [illegible]

S/[illegible]
B001/B066

AUTHORS: Kolyaskina, Z. N. and Petrov, A. A.

TITLE: Reactions of Chlorine-containing Telomers of Diene Hydrocarbons. IV. Reactions of 1-Chloro-5,5-dimethyl Hexene-2 and 1,3-Dichloro-5,5-dimethyl Hexene-2 With Sodium Acetoacetic Acid- and Sodium Malonic Acid Esters

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, No [illegible], pp 3243 - 3247

TEXT. For the purpose of using the adducts of tertiary halogen derivatives on diene compounds in organic synthesis the authors investigated the reactions of 1-chloro-5,5-dimethyl hexene-2 and 1,3-dichloro-5,5-dimethyl hexene-2 with sodium acetoacetic and sodium malonic acid esters. Following Ref. 2 the authors show that under ordinary conditions unsaturated ketones with quaternary carbon atoms at the end of the chain are obtained from both chlorides and sodium acetoacetic ester according to the Scheme

Card 1/3

Reactions of Chlorine-containing Telomers of Diene Hydrocarbons. IV. Reactions of 1-Chloro-5,5-dimethyl Hexene-2 and 1,3-Dichloro-5,5-dimethyl Hexene-2 With Sodium Acetoacetic Acid and Sodium Malonic Acid Esters

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B00[illegible]/B066

$(CH_3)_3CCH_2CX{=}CHCH_2Cl \longrightarrow (CH_3)_3CCH_2CX{=}CHCH_2CH_2COCH_3$

(I) X = H, (II) X = Cl. These ketones are colorless oils insoluble in water, of pleasant odor, readily forming crystalline products with hydrazine derivatives. Two frequencies in the infrared spectrum of the ketones indicate the presence of a double bond, and in the spectrum of the ketone (I) there is one frequency to be assigned to the group -CH=CH-(trans). The frequencies of a vinyl group are missing. In condensation of the same chlorides with sodium malonic ester the corresponding alkenyl malonic acid esters result, but with lower yields (Scheme 2). Like in the reaction with sodium acetoacetic ester, that with sodium malonic ester takes place without allyl rearrangement. In the infrared spectra of the esters (III) and (V), as well as of the acids (IV) and (VI), the characteristic deformation frequencies of the vinyl group are absent (Fig.). The spectra of the ester (III) and of the acid (IV) show sufficiently intense frequencies of the group -CH=CH-. Their semicarbazones were synthesized in crystalline form as

Reactions of Chlorine-containing Telomers of Diene Hydrocarbons. IV. Reactions of 1-Chloro-5,5-dimethyl Hexene [illegible] and 1,3 Dichloro-5,5-dimethyl Hexene- With Sodium Acetoacetic Acid- and Sodium Malonic Acid Esters

S/[illegible]
[illegible]

derivatives of the resultant ketones, and their amides as derivatives of the resultant acids. There are [illegible] figures and [illegible] Soviet references

ASSOCIATION: Leningradskiy tekhnologicheskiy institut imeni Lensoveta (Leningrad Technological Institute imeni Lensoveta)

SUBMITTED: October 25, [illegible]

Card 3/3

S/079/60/030/[illegible]
B001/B066

AUTHORS: Bal'yan, Kh. V., Petrov, A. A., Borovikova, N. A., Kormer, V. A. and Yakovleva, T. V.

TITLE: Hydrogenation of Unsaturated Compounds in the Presence of Colloidal Palladium. XIV. Some Peculiarities of the Hydrogenation of Bisubstituted Allene Hydrocarbons

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 10, pp. 3247 - 3253

TEXT: There are only few data available in publications concerning special cases of the hydrogenation of seven bisubstituted allenes (Table). In the present paper, the authors study some rules governing the hydrogenation of the following bisubstituted allene hydrocarbons: octadiene-3,4; nonadiene-3,4; decadiene-3,4; 7-methyl octadiene-2,3; 7-methyl octadiene-3,4; 6,6-dimethyl heptadiene-2,3; and 7,7-dimethyl octadiene-3,4. It was found that the first hydrogen mole is usually added at an increasing rate, after which hydrogenation slows down considerably (Diagram 1). In hydrocarbons of isostructure this rule

Card 1/3

Hydrogenation of Unsaturated Compounds in the
Presence of Colloidal Palladium. XIV. Some
Peculiarities of the Hydrogenation of Bisubstituted
Allene Hydrocarbons

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B001/B066

manifests itself still more distinctly. The hydrogenation of allenes takes place selectively, and when taking up half of the calculated hydrogen quantity, a mixture of olefins with a double bond in position 2-, 3-, or 4- is formed. Allene hydrocarbon reacts completely in this case. Alkenyl allenes (octatriene-1,3,4; decatriene-1,3,4; 2-methyl octatriene-1,3,4; 8-methyl nonatriene-1,3,4) are hydrogenated in the same way. After taking up about 2 moles of hydrogen, the reaction rate decreases rapidly. Allenes and hydrocarbons having a double bond in the end position disappear completely or to a considerable extent after taking up the first hydrogen mole. The infrared spectra of the hydrogenation products of allenes with 50% of the hydrogen quantity are not indicative of allene compounds (Diagram 2). Diagram 1 does not show any characteristic differences of the hydrogenation rates of 2,3- and 3,6-dienes. Diagram 3 shows curves for the hydrogenation rates of alkenyl allenes; Diagram 4 shows the infrared spectra of the hydrogenation products of alkenyl allenes in a hydrocarbon/hydrogen ratio [illegible]

Card 2/3

Hydrogenation of Unsaturated Compounds in the Presence of Colloidal Palladium XIV Some Peculiarities of the Hydrogenation of Bisubstituted Allene Hydrocarbons

S/07[illegible]/6[illegible]/0[illegible]/0[illegible]/0[illegible]/0[illegible]
B00[illegible]/B066

The investigation results thus indicate that the hydrogenation of bi-substituted allenes takes place selectively, and is similar to the hydrogenation of acetylenes having the acetylene group in the end position. In the case of alkenyl allenes, the direction of hydrogenation depends to a certain extent on the hydrocarbon structure. There are 4 figures, 2 tables, and 9 Soviet references.

ASSOCIATION: Leningradskiy tekhnologicheskiy institut im. Lensoveta (Leningrad Technological Institute imeni Lensovet)

SUBMITTED: October 2[illegible], 1959

Card 3/3

[illegible]

S/079/60/030/011/005/026
[illegible]

AUTHORS: Shvarts, Y., [illegible] and Petrov, A. A.

TITLE: Reactions of Chlorine-containing Telomers of Diene Hydrocarbons. V. Synthesis of Some Alcohols of the Sesquiterpene Series and Their Analogs

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 11, pp. 3598-3604

TEXT: In the present paper, terpene, sesquiterpene, and polyterpene
chlorides were applied to the synthesis of nerolidol, farnesol, and their
analogs and homologs according to the classical method by L. Ružicka. The
study utilized the terpene chlorides obtained by telomerization of prenyl
chloride with isoprene (geranyl chloride) and piperylene hydrochloride
with isoprene and chloroprene (Ref. 15). Geranyl acetone resulted from
geranyl chloride, and from the former, dehydronerolidol, nerolidol, and
farnesol were obtained. Dehydronerolidol had to be freed from ketone im-
purities. This fact, which is confirmed only by spectroscopic investigation,
indicates that the purity of many sesquiterpene alcohols described in

Card 1/3

Reactions of Chlorine-containing Telomers of Diene Hydrocarbons. V. Synthesis of Some Alcohols of the Sesquiterpene Series and Their Analogs

86500

S/0[illegible]/60/030/0[illegible]

B00[illegible]/B0[illegible]

publications is insufficient without checking their infrared spectra. In analogous manner, the isomers of dehydronerolidol and nerolidol were obtained from 1-chloro-3,7-dimethyl-octadiene-2,6, i.e., 3,7,9-trimethyl-dodecadien-6,10-in-1-ol-3 and 3,7,9-trimethyl-dodecatrien-1,6,10-ol-3. The analogs of the above-mentioned products with one chlorine atom instead of the methyl group, 7-chloro-3,9-dimethyl-dodecadien-6,10-in-1-ol-3 and 7-chloro-3,9-dimethyl-dodecatrien-1,6,10-ol-3 resulted from 1,7-dichloro-5-methyl-octadiene-2,6. These alcohols are colorless, oily liquids with pleasant odor, and distillable without decomposition. In the infrared spectra of the alcohols, a weak 2120 cm^{-1} band is assignable to the triple bond in the end position, and an intense 3290 cm^{-1} band to the stretching vibrations of the CH group. The valence frequencies of the double bond in the spectra of alcohols (without chlorine) show a weak intensity. The deformation vibrations of the CH group in the grouping -CH=CH- show an intense frequency. In alcohols with a nerolidol grouping, intense deformation frequencies [illegible] and [illegible] cm^{-1} are indicative of a vinyl group. There are [illegible] figure, [illegible] table, and [illegible] references: 1[illegible] Soviet, 1 US, [illegible] Swiss,

Card 2/3