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RESEARCH ARTICLE

Synthesis and reactions of alkenyl-*gem*-dichlorocyclopropanes obtained from piperylene

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Objectives. *This study aims to obtain alkenyl-gem-dichlorocyclopropanes from piperylene. The products are then subjected to thermocatalytic isomerization and hydrogenation.*
Methods. *To determine the qualitative and quantitative composition of the reaction crudes, the following analytical methods were used: gas-liquid chromatography using the Crystal 2000 hardware complex, mass spectrometry using a Chromatec-Crystal 5000M device with the NIST 2012 database, and nuclear magnetic resonance (NMR) spectroscopy using a Bruker AM-500 device at operating frequencies of 500 and 125 MHz.*
Results. *Alkenyl-gem-dichlorocyclopropanes were synthesized in the presence of triethylbenzyl ammonium chloride as catalyst. Their isomerization and hydrogenation gave the corresponding gem-dichlorocyclopentene and isomers of alkyl-gem-dichlorocyclopropanes. The structure of synthesized substances were analyzed by gas-liquid chromatography, mass spectrometry, and NMR spectroscopy.*
Conclusions. *The results show that formation of four isomeric substituted gem-dichlorocyclopropanes occurs in high yield during incomplete dichlorocyclopropanation of piperylene. The thermocatalytic isomerization of substituted gem-dichlorocyclopropanes in the presence of SAPO-34 zeolite leads to the formation of one product, i.e., gem-dichlorocyclopentene, and hydrogenation of substituted gem-dichlorocyclopropanes in the presence of Pd/C catalyst gives three isomeric alkyl-gem-dichlorocyclopropanes.*

Keywords: *alkenyl-gem-dichlorocyclopropane, isomerization, hydrogenation, SAPO-34 zeolite, Pd/C catalyst*

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НАУЧНАЯ СТАТЬЯ

Синтез и реакции алкенил-*гем*-дихлорциклопропанов на основе пиперилена

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Цели. *Получить алкенил-гем-дихлорциклопропаны на основе пиперилена, провести их термокаталитическую изомеризацию и гидрирование.*
Методы. *Для определения качественного и количественного состава реакционных масс использованы следующие методы анализа: газожидкостная хроматография (на аппаратно-программном комплексе «Кристалл 2000»), хроматомасс-спектрометрия (на приборе «Хроматэк-Кристалл 5000М» с базой NIST 2012) и спектроскопия ядерного магнитного резонанса (ЯМР) (на приборе «Bruker AM-500» с рабочими частотами 500 и 125 МГц).*
Результаты. *Алкенил-гем-дихлорциклопропаны синтезированы в присутствии катализатора триэтилбензиламмоний хлористый. Дальнейшей их изомеризацией и восстановлением получены соответствующие гем-дихлорциклопентен и изомеры алкил-гем-дихлорциклопропанов. Строение синтезированных веществ проанализировано и доказано методами газожидкостной хроматографии, масс-спектрометрии и ЯМР-спектроскопии.*
Выводы. *Установлено, что неполное дихлорциклопропанирование пиперилена протекает количественно с образованием четырех изомерных замещенных гем-дихлорциклопропанов, при термокаталитической изомеризации которых в присутствии цеолита SAPO-34 происходит образование одного продукта – гем-дихлорциклопентена, а при их восстановлении с помощью катализатора Pd/C наблюдается образование трех изомерных алкил-гем-дихлорциклопропанов.*

Ключевые слова: *алкенил-гем-дихлорциклопропаны, изомеризация, гидрирование, SAPO-34, Pd/C*

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INTRODUCTION

Substituted three-membered carbocycles, in particular, *gem*-dichlorocyclopropanes, are widely used in the chemistry of natural and medicinal substances [1–8]. The most effective route for the synthesis of *gem*-dihalocyclopropanes is based on the [2 + 1]-cycloaddition of dichlorocarbenes at multiple bonds [9–18]. Following this method, from industrial dienes such as divinyl, isoprene, and 2,3-dimethyl-butadiene, the corresponding alkenyl-*gem*-dichlorocyclopropanes are obtained, which are used in fine organic synthesis [19, 20]. In this context, the purpose of this study is to perform the dichlorocarbenation of piperylene as a large-tonnage diene and to conduct a series of conversions of the corresponding alkenyl-*gem*-dichlorocyclopropanes.

MATERIALS AND METHODS

Analysis of the reaction crudes was performed using gas-liquid chromatography on the hardware-software complex Crystal 2000, *NPF Meta-khrom*, Russia. Mass spectra were obtained using a *Chromatec-Crystal 5000M* instrument (*Chromatec*, Russia) with the NIST 2012 database (*National Institute of Standards and Technology*, USA). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-500 spectrometer (*Bruker Corporation*, USA) at operating frequencies of 500 and 125 MHz, respectively, using $CDCl_3$ as solvent. Chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. Spin–spin coupling constants (*J*) are given in Hz.

Substituted vinyl-*gem*-dichlorocyclopropanes **2a,b** and **3a,b** were obtained following a reported procedure [19], using chloroform, 50% alkali solution, and triethylbenzylammonium chloride as an interphase catalyst.

1,1-Dichloro-2-((1-*Z*)-prop-1-en-1-yl)-cyclopropane (2a). Colorless liquid. Yield (**2** + **3**): 95%, T_{boil} = 48–50°C (35 mm Hg). ^1H NMR spectrum ($CDCl_3$), δ (ppm), *J* (Hz): 1.20 d (1H, CHa, $J = 5.3$), 1.72 d (1H, CHb $J = 5.3$), 1.75 t (3H, CH_3, $J = 3.1$), 2.38–2.43 m (1H, CH), 5.15 t (1H, CH, $J = 6$), 5.20–5.25 m (1H, CH). ^{13}C NMR ($CDCl_3$), δ_C (ppm): 14.39 (CH_3), 27.42 (CH_2), 28.72 (CH), 61.09 (C), 126.11 (CH), 128.97 (CH). Mass spectrum, *m/e* (I_{rel}, %): 150/152/154 (≤3) [M^+], 135/137/139 (≤5), 115/117 (44/12), 99/101 (22/8), 79/100, 77/65.

1,1-Dichloro-2-((1-*E*)-prop-1-en-1-yl)-cyclopropane (2b). Colorless liquid. Yield (**2** + **3**): 95%, T_{boil} = 48–50°C (35 mm Hg). ^1H NMR ($CDCl_3$), δ (ppm), *J* (Hz): 1.20 d (1H, CHa, $J = 5.3$), 1.72 d (1H, CHb, $J = 5.3$), 1.75 t (3H, CH_3, $J = 3.1$), 2.08–2.12 m (1H, CH), 5.28–5.35 m (1H, CH), 5.37 d (1H, CH, $J = 13.7$). ^{13}C NMR ($CDCl_3$), δ_C (ppm): 18.03 (CH_3), 28.39 (CH), 27.69 (CH_2), 61.09 (C), 126.63 (CH), 130.12 (CH). Mass spectrum, *m/e* (I_{rel}, %): 150/152/154 (≤4) [M^+], 135/137.139 (≤5), 115/117 (42/12), 99/101 (20/10), 79/100, 77/72.

***cis*-1,1-Dichloro-2-vinyl-3-methylcyclopropane (3a).** Colorless liquid. Yield (**2** + **3**): 95%, T_{boil} = 48–50°C (35 mm Hg). ^1H NMR ($CDCl_3$), δ (ppm), *J* (Hz): 1.42 s (1H, CH), 1.35 t (3H, CH_3, $J = 7.8$), 2.20–2.30 m (1H, CH), 5.45–5.60 m (2H, CH_2), 5.75 dd (1H, CH, $J = 10, 13$). ^{13}C NMR ($CDCl_3$), δ_C (ppm): 9.68 (CH_3), 31.90 (CH), 35.91 (CH), 61.09 (C), 120.11 (CH_2), 134.32 (CH). Mass spectrum, *m/e* (I_{rel}, %): 150/152/154 (≤4) [M^+], 135/137/139 (≤5), 115/117 (36/12), 99/101 (20/8), 79/100, 77/70.

***trans*-1,1-Dichloro-2-vinyl-3-methyl-cyclopropane (3b).** Colorless liquid. Yield (**2** + **3**): 95%, T_{boil} = 48–50°C (35 mm Hg). ^1H NMR ($CDCl_3$), δ (ppm), *J* (Hz): 1.11 d (1H, CH, $J = 10$), 1.52 t (3H, CH_3, $J = 6.8$), 2.20–2.30 m (1H, CH), 5.45–5.60 m (2H, CH_2), 5.75 dd (1H, CH, $J = 10, 13$). ^{13}C NMR ($CDCl_3$), δ_C (ppm): 9.68 (CH_3), 33.15 (CH), 40.19 (CH), 61.09 (C), 118.29 (CH_2), 134.32 (CH). Mass spectrum, *m/e* (I_{rel}, %): 150/152/154 (≤8) [M^+], 135/137/139 (≤8), 115/117 (46/26), 99/101 (22/10), 79/100, 77/72.

Isomerization was conducted in a fixed-bed flow-through unit in a reactor with a volume of 15 cm^3, at atmospheric pressure, and at a temperature ranging from 130 to 280°C. SAPO-34 zeolite (made in China) was used as a catalyst, which was activated in a flow of hydrogen at 550°C for 5 h before use. Raw materials (50 mL of a mixture of vinyl-*gem*-dichlorocyclopropane : decane in a 1 : 2 volume ratio) were supplied using a pump. The product of the catalysis was dried with freshly calcined calcium chloride and evaporated under a weak vacuum after filtering off the salt to give 4.

4,4-Dichloro-3-methylcyclopentene (4). Colorless liquid. Yield: 94%, T_{boil} = 57°C (35 mm Hg). ^1H NMR ($CDCl_3$), δ (ppm), *J* (Hz): 1.35 t (3H, CH_3, $J = 7.0$), 2.53 d (1H, CHa, $J = 3.9$), 2.85 t (1H, CHb, $J = 3.6$), 5.56 t (1H, CH, $J = 6$), 5.88 d (1H, CH, $J = 5.9$). ^{13}C NMR ($CDCl_3$), δ_C (ppm): 14.99 (CH_3), 53.22 (CH_2), 62.68 (CH_2), 81.16 (C), 124.92 (CH=), 141.06 (C=). Mass spectrum, *m/e* (I_{rel}, %): (150/152/154)/35/16/5 [M^+], (115/117)/(100/34), (77/79)/(89/55), 51/27.

For *hydrogenation*, palladium on carbon (Pd/C), granular, TU 2170-300-29131036-97[1], was used as a catalyst. The catalyst was ground in a mortar before use, sieved, and stored in a box in an extractor. A calculated amount of Pd/C catalyst, which was finely ground in a mortar and weighed on an analytical balance, was loaded into the reactor (Fig. 1). A solution containing a mixture of dichlorocyclopropanes **2a,b** and **3a,b** in ethyl-acetate (20 mL) with a mass concentration of 50 g/L was added. From hydrogen generator 6, buffer tank 7 was filled with hydrogen by opening valve 1 and closing valve 2. Valve 1 was then closed, and valves 2–4 were open, while maintaining mixing device 11 turned off and vessel 10 completely filled with liquid. Thus, the system was purged with hydrogen. Then, valves 4 and 3 were sequentially closed, and with valve 5 open, cylindrical vessel 8 was filled with hydrogen from the buffer tank to the lower mark, creating a slight excess pressure of the water column from pressure reservoir 9. Then, valve 2 was closed, valve 3 was open, and the stirring device was turned on, setting the preset mixing speed. The progress of the reaction was monitored by determining the volume of absorbed hydrogen. The experiment was continued until a noticeable decrease in the rate of hydrogen absorption was observed.

After hydrogenation, the following products were obtained:

1,1-Dichloro-2-propylcyclopropane (5). Colorless liquid. Yield (**5** + **6**): 95%, T_{boil} = 54°C (35 mm Hg). ^1H NMR ($CDCl_3$), δ (ppm), *J* (Hz): 0.95 t (3H, CH_3, $J = 7$), 1.20–1.25 m (6H, 3 CH_2), 1.36–1.55 m (1H, CH). ^{13}C NMR ($CDCl_3$), δ_C (ppm): 15.03 (CH_3), 23.99 (CH_2), 27.06 (CH_2), 31.09 (CH_2), 38.44 (CH), 65.44 (C). Mass spectrum, *m/e* (I_{rel}, %): 152/154/156 (7) [M^+], 123/49, 110/66, 75/5, 87/37, 51/100.

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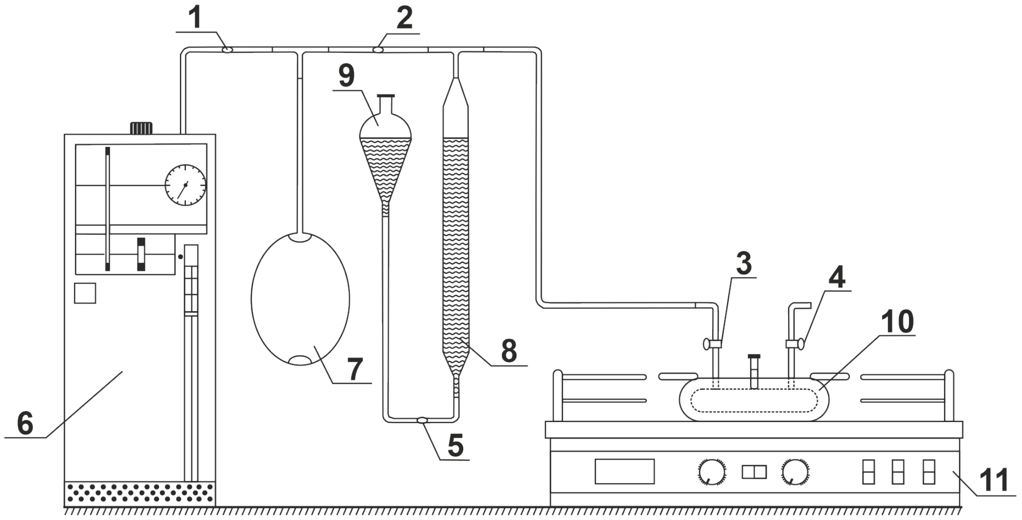
[1] Information about the catalyst is available on the manufacturer's website https://www.kazanorgsintez.ru.



Schematic representation of the installation for hydrogenation at atmospheric pressure. Valves (1–5), hydrogen generator (6), buffer tank (7), cylindrical vessel (8), pressure tank (9), hydrogenation reactor (10), stirring device (11).

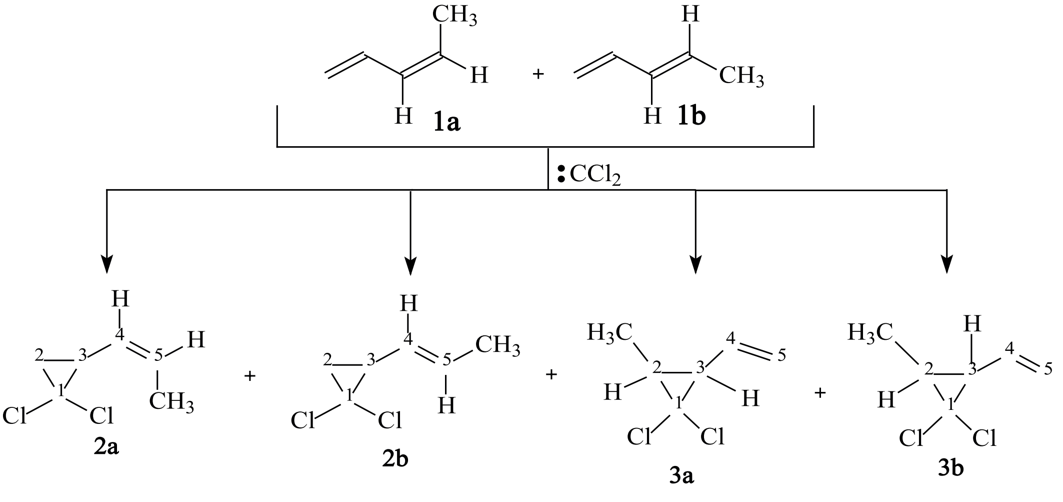
***cis*-1,1-Dichloro-2-methyl-3-ethylcyclopropane (6a).** Colorless liquid. Yield (**5** + **6**): 95%, T_{boil} = 54°C (35 mm Hg). ^1H NMR ($CDCl_3$), δ (ppm), *J* (Hz): 0.90 d (1H, 1 CH, *J* = 7), 1.02 t (3H, CH_3, *J* = 5), 1.45 t (3H, CH_3, *J* = 3), 1.61–1.66 m (1H, CH), 1.78–1.83 m (2H, CH_2). ^{13}C NMR ($CDCl_3$), δ_C (ppm): 10.55 (CH_3), 14.09 (CH_3), 19.44 (CH_2), 32.94 (CH), 34.01 (CH), 67.55 (C). Mass spectrum, *m/e* (I_{rel}, %): 152/154/156 (9) [M^+], 123/59, 110/30, 75/15, 87/67, 51/100.

***trans*-1,1-Dichloro-2-methyl-3-ethylcyclopropane (6b).** Colorless liquid. Yield (**5** + **6**): 95%, T_{boil} = 54°C (35 mm Hg). ^1H NMR ($CDCl_3$), δ (ppm), *J* (Hz): 1.05–1.15 m (1H, CH), 1.02 t (3H, CH_3, *J* = 5), 1.45 t (3H, CH_3, *J* = 3), 1.61–1.66 m (1H, CH), 1.78–1.83 m (2H, CH_2). ^{13}C NMR ($CDCl_3$), δ_C (ppm): 11.01 (CH_3), 15.88 (CH_3), 19.44 (CH_2), 34.71 (CH), 41.39 (CH), 67.67 (C). Mass spectrum, *m/e* (I_{rel}, %): 152/154/156 (7) [M^+], 123/49, 110/66, 75/5, 87/37, 51/100.

RESULTS AND DISCUSSION

At the initial stage of the dichlorocarbenation of commercial piperylene (*cis*-**1a** : *trans*-**1b** = 1 : 4), which was performed according to the Makoshi method [21], carbenes attach to nonequivalent terminal and internal double C=C bonds at different rates, leading to the formation of a mixture of propenyl derivatives **2a,b** and vinyl derivatives **3a,b** in a ratio of 1 : 3, respectively (Scheme 1). This is due to the fact that the methyl substituent located in the α-position activates the double bond with respect to the electron-withdrawing $:CCl_2$ carbene. Note that the 2,2-disubstituted double bond in isoprene is one order of magnitude more active than the unsubstituted one [19].

The observed ratio of stereoisomers **2a** : **2b** = 1 : 4 coincides with the content of *cis*- and *trans* forms in the initial diene **1a,b**. The addition of dichlorocarbene to the



Scheme 1. Carbenation of piperylene **1a,b**.

substituted double bond proceeds nonstereoselectively, and isomers **3a,b** are formed in similar amounts (**3a** : **3b** = 1 : 1.5).

Next, the thermocatalytic isomerization (Scheme 2) of the obtained alkenyl-*gem*-dichlorocyclopropanes **2a,b** and **3a,b** was performed at 230°C according to a previously described method [22] using commercially available SAPO-34 zeolite as a catalyst [23].

4,4-Dichloro-3-methylcyclopentene **4** was obtained in a yield of more than 90% as a result of the opening of the three-membered carbocycles at the C^1–C^3 bonds on the catalyst. No products resulting from the cleavage of the C^2–C^3 bonds were detected.

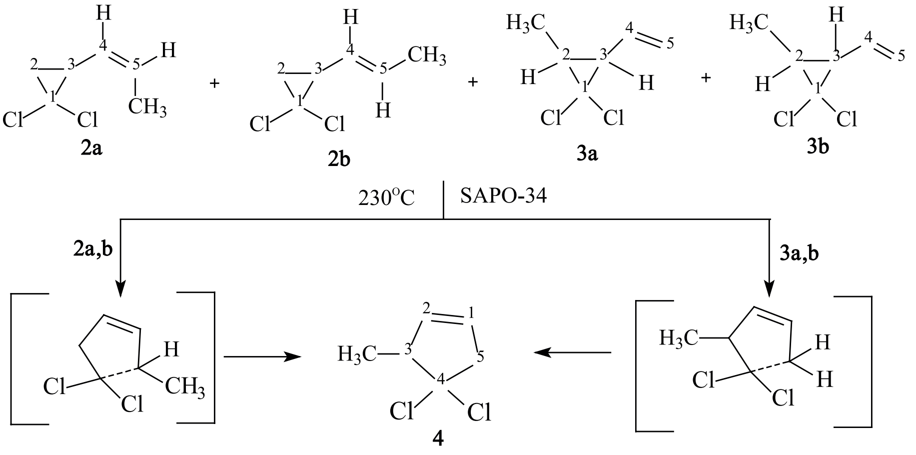
Hydrogenation (Scheme 3) of alkenyl-*gem*-dichlorocyclopropanes **2a,b** and **3a,b** was conducted using commercial Pd/C catalyst [24, 25] at a temperature of 22–24°C and atmospheric pressure for 3.5–4 h.

Under these conditions, a mixture of propyl-*gem*-dichlorocyclopropane **5**, *cis*-2-methyl-3-ethyl-*gem*-dichlorocyclopropane **6a**, and *trans*-2-methyl-3-ethyl-*gem*-dichlorocyclopropane **6b** was obtained quantitatively. The ratio of the latter compounds corresponds to the starting content in the initial mixture of vinyl derivatives (**6a** : **6b** = **3a** : **3b** = 1 : 1.5).

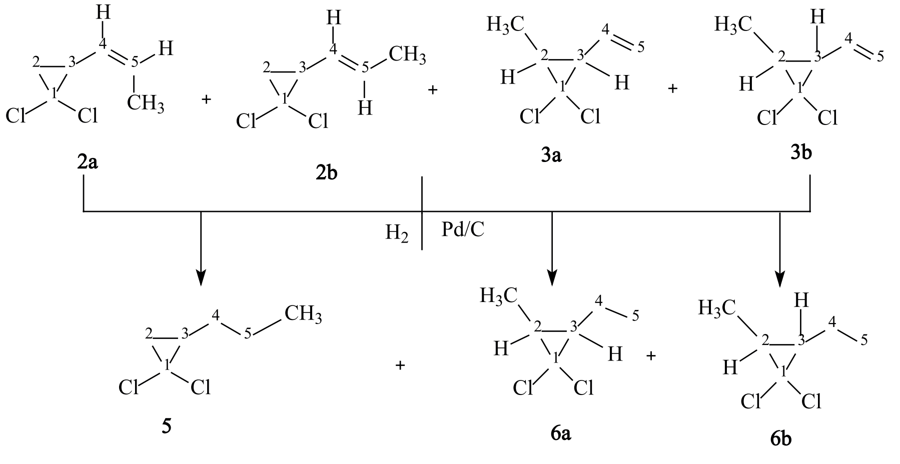
The method of competitive kinetics [26] (maximum conversion of 30%) was used to determine the relative reactivity of propenyl **2a,b** and vinyl derivatives **3a,b** in the hydrogenation reaction. Under the studied conditions[2], judging by the rate of accumulation of products **5** and **6a,b**, vinyl derivatives **3a,b** are two times more active than propenyl derivatives **2a,b**.

The composition of the obtained products **2a,b**, **3a,b**, **5**, **6a,b**, and the isolated compound **4** was established by NMR spectroscopy and gas chromatography–mass spectrometry.

The ^1H NMR spectrum of the mixture of carbenation products **2a,b** and **3a,b** shows the presence of signals of multiple bonds of protons at C^4 and C^5 carbon atoms. For molecule **2a**, the proton at the C^4 carbon atom gives rise to a triplet at 5.15 ppm (^3J = 6 Hz), and that at the C^5 carbon atom affords a



Scheme 2. Isomerization of alkenyl-*gem*-dichlorocyclopropanes **2a,b** and **3a,b.**



Scheme 3. Reduction of alkenyl-*gem*-dichlorocyclopropanes **2a,b** and **3a,b.**

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[2] The starting ratio **2a,b** : **3a,b** = 1 : 3.

multiplet in the range 5.20–5.25 ppm, which is typical for the *cis*-isomer. Meanwhile, for the *trans*-**2b** isomer, the signal of the proton at the C^4 carbon atom appears at 5.28–5.35 ppm, and the proton at C^5 resonates as a doublet at 5.37 ppm (^3J = 13.7 Hz), which confirms the *trans*-configuration of the double bond. In a mixture of compounds **3a** and **3b**, analogous signals of protons at C^4 and C^5 appear as doublet of doublets at 5.75 ppm (^3J = 10 and 13 Hz) and a multiplet at 5.45–5.60 ppm. The protons of the cyclopropane ring at the C^2 the carbon atom for the *cis*-**2a** and *trans*-**2b** isomers appear as two identical doublets at 1.20 ppm (^2J = 5.3 Hz) and 1.72 ppm (^2J = 5.3 Hz). A similar proton signal at the C^2 carbon atom of molecules **3a** and **3b** affords a multiplet at 2.20–2.30 ppm. The proton at the C^3 carbon atom for compound **3a** appears as a singlet at 1.42 ppm, which indicates its *cis*-arrangement, whereas it is high-field shifted to 1.11 ppm and appears as a doublet (^3J = 10 Hz) for compound **3b**, which is typical for the *trans*-configuration of the proton.

In the ^{1}H NMR spectrum of a mixture of hydrogenation products **5** and **6a,b**, the presence of propyl-*gem*-dichlorocyclopropane **5** is evidenced by a triplet signal of the methyl group in the high-field region at 0.95 ppm (^3J = 7 Hz) and a multiplet for two methylene groups of the propyl fragment in the range 1.20–1.25 ppm. The geometric isomers **6a,b** are characterized by the presence of signals attributable to the proton at the C^3 carbon atom conjugated with the ethyl group. Thus, for *cis*-1,1-dichloro-2-methyl-3-ethylcyclopropane **6a**, the proton at the C^3 carbon atom of cyclopropane gives rise to a doublet in the high-field region at 0.90 ppm (^3J = 7 Hz), and for *trans*-1,1-dichloro-2-methyl-3-ethylcyclopropane **6b**, a similar signal appears as a multiplet in the lower region at 1.05–1.10 ppm.

In the ^{13}C NMR spectra of the mixture of alkenyl-*gem*-dichlorocyclopropanes **2a,b** and **3a,b**, the most representative feature is the C^1 signal of the carbon atom at 61.09 ppm. For the *cis*-**2a** isomer, the C^4 and C^5 carbon atoms of the double bond resonate at 126.11 and 128.97 ppm, respectively, whereas for the *trans*-**2b** isomer they appear in lower field, at 126.63 and 130.12 ppm, respectively. For compound **3a**, the presence of high-field signals for the C^2 and C^3 carbon atoms of the cyclopropane ring (31.90 and 35.91 ppm) confirms the *cis*-configuration, whereas the signals at lower field for C^2 and C^3 (33.15 and 40.19 ppm) of molecule **3b** are indicative of the *trans*-configuration of this isomer.

The ^{13}C NMR spectra of a mixture of alkyl derivatives **5** and **6a,b** are characterized by the signals ascribed to the C^1 carbon atoms in the range of 65–67 ppm. The signal of the methyl group of 1,1-dichloro-2-propylcyclopropane **5** appears at 15.03 ppm, whereas those of molecules **6a,b** are high-field shifted to 10.55 and 11.01 ppm, respectively. For compound **6a**, the presence of signals of the C^2 and C^3 carbons of the cyclopropane ring at 32.94 and 34.01 ppm confirms the *cis*-configuration. For molecule **3b**, the signals of C^2 and C^3 atoms appear at lower field (34.71 and 41.39 ppm), indicating the trans configuration of this isomer.

Several pathways can be proposed for the dissociative ionization of a mixture of *gem*-dichlorocyclopropanes **2a,b** and **3a,b**. Thus, the molecule decomposes into a dichlorocyclopropane fragment and the substituent or the molecule loses chlorine atoms while the main carbon skeleton is preserved.

The table shows the values of fission ion mass *m* and the relative intensity of ion peaks *e*, (% of the maximum) for compounds **2a,b** and **3a,b**.

The dissociative ionization of *gem*-dichlorocyclopropanes **6** and **7a,b** and alkenyl-*gem*-dichlorocyclopropanes **2a,b** and **3a,b**, can proceed as follows: the molecule decomposes into a dichlorocyclopropane fragment and a substituent R; alternatively, the molecule loses chlorine atoms while preserving the carbon skeleton.

CONCLUSIONS

The dichlorocarbenation of piperylene by the Makoshi method proceeds quantitatively yielding a mixture of *cis*-, *trans*-1,1-dichloro-2-(prop-1-en-1-yl)cyclopropanes and

Values of fission ion mass *m* and relative intensity of ion peaks *e* (% of maximum) for compounds **2a,b** and **3a,b**

Compound	***m/e* (%)**					
	M+ 150/152/154	**79**	**77**	**115/117**	**99/101**	**135/137/139**
2a	≤3	100	65	44/12	22/8	≤5
2b	≤4		72	42/12	20/10	≤5
3a	≤4		70	36/12	20/8	
3b	≤8		72	46/26	22/10	≤8

cis-, *trans*-1,1-dichloro-2-vinyl-3-methylcyclopropanes. Hydrogenation of the obtained isomeric alkenyl-*gem*-dichlorocyclopropanes over a palladium catalyst (Pd/C) gives 1,1-dichloro-2-propylcyclopropane and *cis*-, *trans*-1,1-dichloro-2-methyl-3-ethylcyclopropanes. *Cis*-, *trans*-1,1-dichloro-2-(prop-1-en-1-yl)cyclopropanes and *cis*-, *trans*-1,1-dichloro-2-vinyl-3-methylcyclopropanes are converted via thermocatalytic isomerization in the presence of SAPO-34 zeolite to 4,4-dichloro-3-methylcyclopentene in a yield of more than 90%.

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Authors' contribution

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G.Z. Raskil'dina – collection and processing of the material, statistical processing;

R.U. Rabaev – consultation on conducting individual stages of the study;

R.R. Daminev – consultation on planning, methodology and implementation of the study;

S.S. Zlotskii – development of the concept of scientific work, critical revision with the introduction of valuable intellectual content.

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