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Catalytic Isomerization of Substituted Vinylcyclopropanes

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Abstract—The catalytic isomerization of substituted vinyl-*gem*-dichlorocyclopropanes in the presence of a series of zeolite catalysts has been studied. It has been shown that substituted *gem*-dichlorocyclopentenes are the sole reaction products. The influence of a number of factors (the type of catalyst, temperature, and reaction time) on the yield of isomerization products has been investigated.

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The reaction of dichlorocarbene with industrial dienes results in vinyl-*gem*-dichlorocyclopropanes in high yields; these compounds are widely used in the synthesis of reagents, oligomers, and polymers [1–5].

In this work, we accomplished for the first time the catalytic isomerization of mono-dichlorocarbenylated olefins **1a**–**1d** into the corresponding *gem*-dichlorocyclopropentenes **2a**–**2d**.

Vinyl-*gem*-dichlorocyclopropanes are known to undergo partial or complete dehydrochlorination at high temperatures (450–550°C), reaction products contain small amounts (≤ 20%) of *gem*-dichlorocyclopropentenes, which are isomeric to the initial compounds [6].

To accomplish the isomerization of vinyl-*gem*-dichlorocyclopropanes **1a**–**1d**, we employed well-known domestic zeolite SAPO-34 [7], which is used in industry for alkane and alkene reforming.

It was found that the catalytic isomerization of compounds **1a**–**1d** at 180–280°C for 1 h leads to the target cyclopentenes **2a**–**2d** in 10–95% yield (selectivity ≥95%) (Scheme 1).

No transformation of compounds **1a**–**1d** was observed even at $T = 280°C$ in the presence of silicon oxide inert under these conditions.

Reaction products contain no 5,5-dichloro derivatives isomeric to cyclopentenes **2a**–**2d**. We explain this fact by the lower strength of the $R^3C–CCl_2$ bond (42–43 kcal/mol) as compared to the $R^3C–CR^1R^2$ bond (49–50 kcal/mol) in the cyclopropane moiety.[1]

Judge by the yield of compounds **2a**–**2d**, 2,2-disubstituted olefins **1b** and **1c** are close in activity to each other and superior to 2-mono derivatives **1a** and **1d** (Fig. 1).

By the example of olefin **1c**, we found that high yield (≥90%) is achieved at 280°C for 1 h and at 230°C for 1.5 h (Table 1).

We revealed that other industrial zeolite reforming catalysts HY [8] and Tseokar-600 [9] also catalyze isomerization of olefins **1a**–**1d** at 280°C, with zeolite HY being equal to SAPO-34, while the yields of compounds **2a**–**2d** in the presence of Tseokar-600 are by factor 1.2–1.5 lower (Fig. 2).

The low efficiency of Tseokar-600 catalyst is likely to be due to its low specific surface (320 m^2/g) as compared with SAPO-34 (630 m^2/g) and HY (600 m^2/g). The presence of Pt atoms on the surface of Tseokar-600 has no effect on the isomerization process.

Thus, the heterogeneous catalytic isomerization of vinyl-*gem*-dichlorocyclopropanes is convenient method for the selective preparation of gem-dichlorocyclopropentenes.

EXPERIMENTAL

Catalysts used in the work were zeolites SAPO-34 (produced at the Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences), HY, and Tseokar-600 (manufactured in the Salavat Catalyst

Table 1. Effect of reaction time on the yield of cyclopentene **2c** in the presence of SAPO-34 catalyst

Contact time, h	Yield (%)		
	180°C	230°C	280°C
0.5	22	45	80
1	38	65	95
1.5	70	90	99

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[1] Bond strength was calculated by the M06-2X/MG3S method [Zhao, Y. and Truhlar, D.G., *J. Chem. Phys.* 2006, vol. 125, no. 19, p. 194101. https://doi.org/10.1063/1.2370993].

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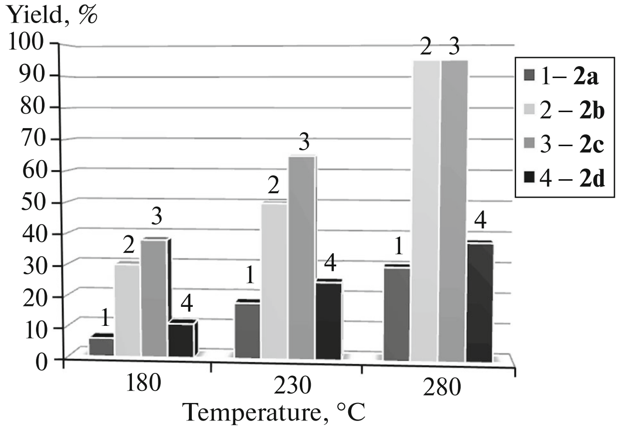


Fig. 1. Catalytic isomerization of substituted vinylcyclopropanes **1a**–**1d** in the presence of SAPO-34 catalyst, contact time 1 h.

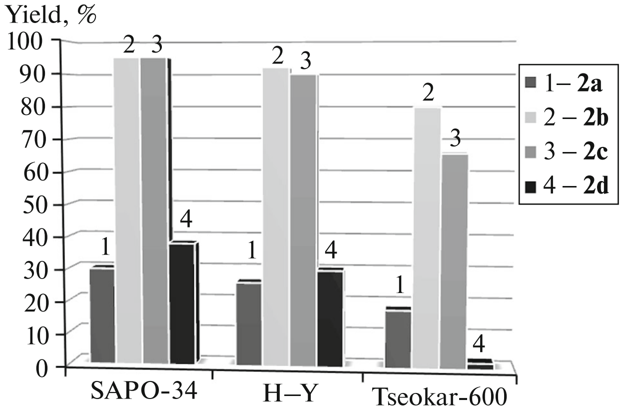


Fig. 2. Catalytic isomerization of substituted vinylcyclopropanes **1a**–**1d** in the presence of different catalysts, contact time 1 h, *t* = 280°C.

Factory, Ltd.). Prior to use, all zeolites were calcined in nitrogen flow at 550°C for 5 h.

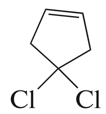
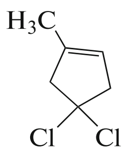
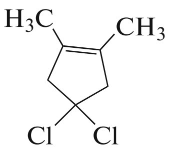
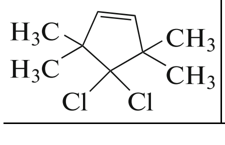
Vinyl-*gem*-dichlorocyclopropanes **1a**–**1d** used in the work were obtained by the known procedures using chloroform, 50% alkali solution, and Katamin AB phase transfer catalyst [11].

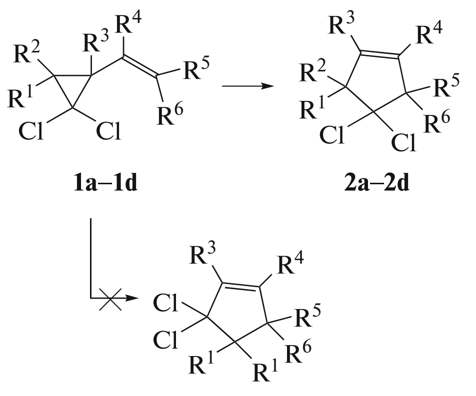
^1H and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer operating at 500 and

Table 2. Characteristics of used catalysts [7, 9, 10]

Catalysts	SiO_2/Al_2O_3, zeolite modulus	Unit cell size, nm	Acidity, meq, H^+/g	Na_2O, %	Pore diameter, Å	Pore volume, cm^3/g	Specific surface area m^2/g
SAPO-34 [7]	22	10	0.06	0.05	3.8	0.27	630
H–Y [9]	6	24	2.1	0.60	0.74	0.56	600
Tseokar-600 (contains Pt) [10]	5	50	0.54	0.1	–	0.5	320

Table 3. Physical characteristics of compounds **2a**–**2d**

Compound (yield, %)	Bp	^1H NMR, ppm	^{13}C NMR, ppm	*m/e*, (I_{rel}, %)
2a (30) 	100°C (760 mmHg)	5.39 (s, 2H, CH=CH, *J* = 8.8). 2.53 (d, 2H, CH_2, *J* = 3.2)	123.39 (CH=CH), 53.29 (2 CH_2), 139.51 (C=)	(138/140/142)/35/16/5 M^+, (115/117)/(100/32), (77/79)/(44/12), (51)/(39)
2b (95) 	42°C (60 mmHg)	1.35 (s, 3H, CH_3), 2.53 (d, (2H, $CH_{2,}$ J = 3.9), 2.85 (d, 2H, CH_2, *J* = 3.9), 5.67 (s, 1H, CH)	17.37 (CH_3), 53.22 (CH_2), 61.68 (CH_2), 81.16 (C), 124.92 (CH=), 140.06 (C=)	(152/154/156)/35/16/5 M^+, (115/117)/(100/34) , (77/79)/(87/26), (51)/(25)
2c (95) 	83°C (20 mmHg)	1.29 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 3.10 (s, 2H, CH_2), 3.18 (s, 2H,CH_2)	16.26 (CH_3), 18.43 (CH_3), 54.88 (CH_2), 59.70 (CH_2), 82.01 (C), 138.52 (C=)	(164/166/168)/20/14/3 M^+, (129/131)/(100/30) , 93/97, (77/79)/(70/15), (51)/(20)
2d (36) 	76°C (10 mmHg)	1.25 (s, 12H, 4 CH_3), 5.39 (s, 2H, CH=CH, *J* = 8.9)	28.19 (4 CH_3), 52.60 (C), 86.37 (C), 137.23 (CH=CH)	(194/196/198)/11/9/2 M^+, (157/159)/(100/5), 82/14, (77/79)/(50/9), (41)/(16)



$R^1, R^2, R^3, R^4, R^5, R^6 = H$ (**1a**, **2a**)
$R^1, R^2, R^3, R^5, R^6 = H, R_3 = CH_3$ (**1b**, **2b**)
$R^1, R^2, R^4, R^5 = H, R^3, R^4 = CH_3$ (**1c**, **2c**)
$R^3, R^4 = H, R^1, R^2, R^5, R^6 = CH_3$ (**1d**, **2d**)

Scheme 1.

125 MHz, respectively, in $CDCl_3$ solutions using TMS as an internal reference. Chemical shifts are given in the δ scale relative to the TMS internal reference. Spin-spin coupling constants (*J*) are given in hertzs.

Mass spectra were obtained on a Kristall-5000M instrument. Analysis conditions: capillary column 30 m long, column temperature from 80 to 280°C, transition line temperature 300°C, ion source temperature 300°C. Temperature was increased at the rate 20 K/min. Helium as a carrier gas.

The isomerization was carried out in a flow reactor with a fixed-bed catalyst. Reactor volume 30 cm^3, atmospheric pressure, temperature range from 180 to 280°C. The raw material (50 mL of a mixture of vinyl-*gem*-dichlorocyclopropane with decane in the volume ratio 1 : 3) was supplied with a pump. The obtained catalysate was dried with freshly calcined calcium chloride, the salt was separated by filtration, and the filtrate was evaporated under slightly reduced pressure (except for **2a**). Table 3 shows the physical constants of compounds **2a**–**2d**.

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