METATHESIS OF DIALKENYLSILANES AND POLYMERIZATION OF 1,1-DIMETHYL-1-SILA-3-CYCLOPENTENE IN PRESENCE OF ALUMINUM–RHENIUM CATALYSTS*

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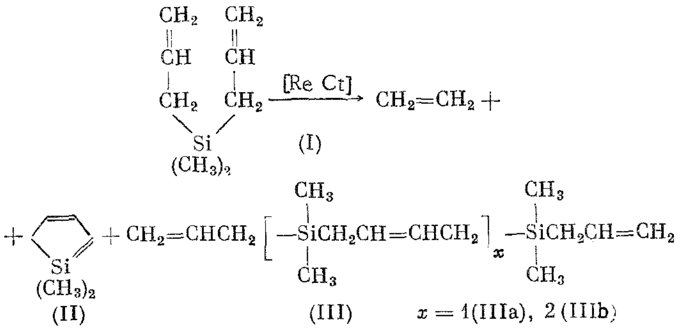
The metathesis (disproportionation) reaction of unsaturated compounds has been studied in detail for hydrocarbons of variable structure (in particular, for unconjugated dienes), and also in the series of functional derivatives of olefins [2, 3]. We studied the metathesis of some dialkenyl derivatives of the Group IVB elements. The formation of unsaturated element–carbon heterocycles (intramolecular metathesis) and heterochain oligo- or polymeric products (intermolecular metathesis) could be expected in this case.

As the catalysts we selected the aluminum–rhenium systems, which have a high activity in the metathesis of various olefin derivatives [4, 5]. As the substrates we used the dialkenylsilanes: dimethyldiallylsilane (I), diallylsilacyclobutane (IV), and dimethylallylbutenylsilane (VII). The transformations were studied in the liquid phase in n-heptane in an argon atmosphere. It proved that the indicated silicoolefins actively eliminate ethylene in the presence of Re_2O_7/Al_2O_3 at 40-100°C. In the case of (I) the reaction proceeds by the scheme:



The results of some of the experiments on the metathesis of (I) are summarized in Table 1.

The structure of (II) was identified via chromatography and mass spectrometry by comparing with the standard, which was obtained by the methylation of 1,1-dichloro-1-sila-3-cyclopentene. Compounds (IIIa, b) were characterized via the PMR and mass spectra. The peak of the molecular ion (MI) is absent in the mass spectrum of (IIIa). The peak with m/z 211 has the highest mass number, while the peak with m/z 299 is the principal peak in intensity. Apparently, the first corresponds to the ion $[M-(CH_2-CH=CH_2)]^+$, and the second to the ion $[Si(CH_3)_2CH_2-CH=CH_2]^+$. In its character the mass spectrum of (IIIb) is close

TABLE 1

Expt. No.	Catalyst	(I):heptane (mole ratio)	T., °C	Time, h	Conversion, %	Yield of products, %		
						(II)	(IIIa)	(IIIb)
1	Re_2O_7/Al_2O_3	1:1	45	3	62	2	50	10
2	$Re_2O_7/Al_2O_3-SnBu_4$	1:1	45	3	78	8	67	2
3	$Re_2O_7/Al_2O_3-SnBu_4$	1:10	45	3	72	12	58	1

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*See [1] for preliminary communication.

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 641-645, March, 1981. Original article submitted April 29, 1980.

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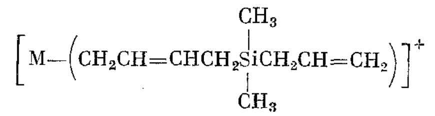
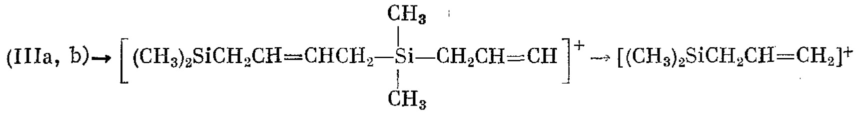
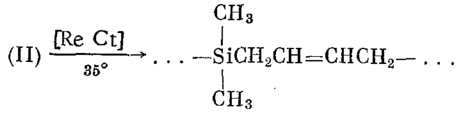
to that of (IIIa). The MI peak is also absent in it; the peak with the highest mass number with m/z 211 corresponds to the fragment  $[M-(CH_2CH{=}CHCH_2Si(CH_3)_2CH_2CH{=}CH_2)]^+$, while the principal peak in intensity with m/z 99 corresponds to the ion $[Si(CH_3)_2CH_2{-}CH{=}CH_2]^+$. The common character of the spectra of (IIIa) and (IIIb), which has a much lower chromatographic mobility, is determined by the similarity of their structure and, consequently, by the common direction of the fragmentation that takes place under electron impact at the $Si{-}C_{alk}$ bonds.



$$\text{(IIIa, b)} \rightarrow [(CH_3)_2SiCH_2CH{=}CHCH_2{-}Si(CH_3)_2{-}CH_2CH{=}CH]^+ \rightarrow [(CH_3)_2SiCH_2CH{=}CH_2]^+$$

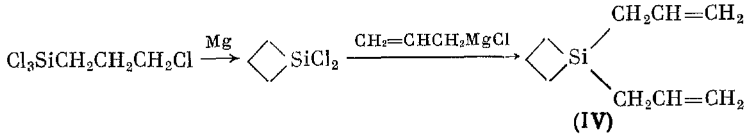
As can be seen from the data in Table 1, the total conversion of (I) increases when $SnBu_4$ is used as the promoter. An increase in the solvent concentration in the starting mixture up to 90% leads to an increase in the yield of (II) up to 12%. The absence of noticeable amounts of heavy polysilicohydrocarbons in the metathesis products of (I) testifies to the inability of the formed (II) to undergo secondary polymerization under the conditions of Expts. 1-3. By special experiments it was shown by us that (II), taken as the starting compound, polymerizes in the presence of Re_2O_7/Al_2O_3 and $Re_2O_7/Al_2O_3{-}SnBu_4$ to give a linear polysilapentenomer (30-35% yield) with mol. wt. 5500 (ebulliometrically in benzene).



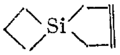
$$\text{(II)} \xrightarrow[35°]{[\text{Re Ct}]} \ldots{-}Si(CH_3)_2CH_2CH{=}CHCH_2{-}\ldots$$

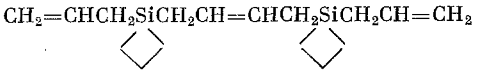
A similar polymerization was reported previously [6], which proceeds in the presence of the homogeneous system $WCl_6{-}Al(i\text{-}Bu)_3{-}Na_2O_2$, and a polymer from the Ge analog of (II), namely 1,1-dimethyl-1-germa-3-cyclopentene, was obtained recently on the system $(CO)_5W{:}C(OMe)Ph{-}TiCl_4$ [7]. The inertness of (II) toward polymerization under the conditions of its synthesis from (I) can be related to the low concentrations of (II) in the reaction mixture, and also to the progress of active competing metathesis and cometathesis reactions involving (I).

The behavior of (IV), synthesized by the scheme



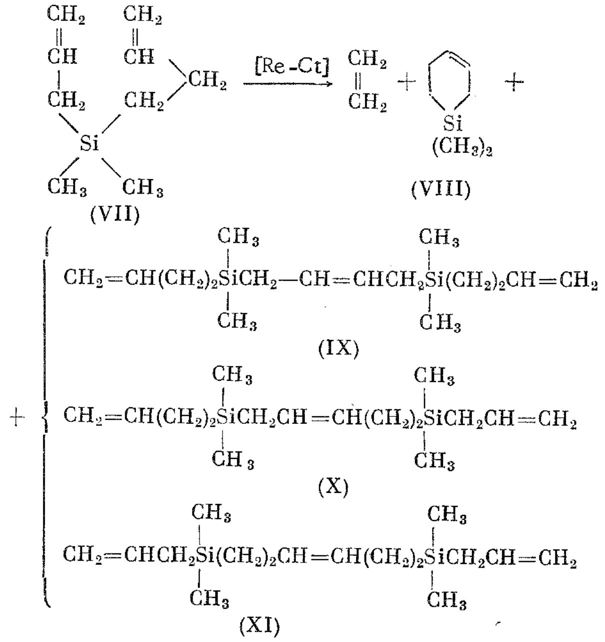
(IV)

was studied under the conditions of Expt. 2. It proved that the metathesis of (IV) under the indicated conditions is possible, despite the presence of a four-membered ring that is inclined to cleave. In the catalyzate, together with undistillable waxy products (35% yield), were recorded by chromatographic mass spectrometry the presence of 4-silaspiro[3,4]-6-octene (V)  (5% yield) and a silicohydrocarbon, which was formed by intermolecular metathesis (∿25% yield):

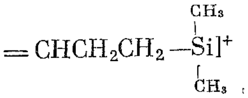
 (VI)

The peaks of the MI with m/z 124 and 276 were respectively observed in the mass spectra of (V) and (VI). The direction of the fragmentation in both cases is determined by the elimination of an ethylene molecule, which is characteristic for silacyclobutane structures [8]. The spectrum of spiran (V) has a peak with m/z 96, which corresponds to the $[M{-}C_2H_4]^+$ ion, while the spectrum of (VI) has peaks with m/z 248 $[M{-}C_2H_4]^+$, 235 $[M{-}(CH_2CH{=}CH_2)]^+$, 207 $[M{-}(CH_2CH{=}CH_2){-}C_2H_4]^+$ and $[CH_2{=}CHCH_2{-}Si$ ◇$]^+$.

Compound (VII) under the conditions of Expt. 2 (see Table 1) displayed a clearly expressed tendency to cyclize via intramolecular metathesis.



At a total (VI) conversion of 80% the yield of 1,1-dimethyl-1-sila-3-cyclohexene (VIII) was 74%, while the total yield of the linear intermolecular metathesis products was ∿4%, with a ratio of (IX):(X):(XI) = 1:2:1. Compound (VIII) was isolated by fractional distillation and was characterized via the PMR and mass spectra. The mass spectrum of (VIII) has an intense peak of the MI (m/z 126), while the principal peak corresponds to m/z 98 ($[M-C_2H_4]^+$). The ejection of a butadiene molecule and appearance of the corresponding peak with m/z 72 is very characteristic for the given compound.



For (XI) and (X) the principal peaks with m/z 113 correspond to the $[CH_2{=}CHCH_2CH_2{-}\overset{CH_3}{\underset{CH_3}{Si}}]^+$ ions, which arise due to cleavage of the $Si-C_{alk}$ bridge bonds. In contrast to them, in the mass spectrum of (XI) the principal peak with m/z 99 is $[CH_2{=}CH{-}CH_2Si(CH_3)_2]^+$. The cleavage of the terminal allyl groups is characterized in the spectra of (X) and (XI) by the peaks with m/z 239 $[M-(CH_2-CH=CH_2)]^+$. In the spectrum of (IX), which lacks terminal allyl groups, this peak is absent.

The obtained data on the metathesis of dialkenylsilanes testify to the fact that the main direction of the reaction is determined by the ring size of the formed heterocycles. The diallyl derivatives of silicon react predominantly by the intermolecular scheme, while (VII) reacts by the intramolecular scheme to give an unstrained six-membered ring. The low yields of (II) can be related both to energetically unfavorable closure to a five-membered ring and to opening of the latter due to secondary cometathesis of (II) and the starting (I).

EXPERIMENTAL

Dimethyldiallylsilane (I) was obtained as described in [9], bp 137°; d_4^{20} 0.7680; n_D^{20} 1.4420.

(Chloromethyl)dimethylallylsilane (XII). To a solution of allylmagnesium chloride [from 31.2 g (1.3 g-atom) of Mg and 100 g (1.3 moles) of allyl chloride (AC) in 500 ml of THF], which had been filtered through a glass filter in an argon atmosphere, was added at 40°C a solution of 143 g (1 mole) of $ClCH_2Si(CH_3)_2Cl$ in 100 ml of THF. The mixture was heated for 1.5 h at 60°, cooled, and decomposed with water and 5% HCl solution. After the usual workup and fractional distillation we obtained 75.6 g (51%) of (XII) with bp 153°; n_D^{20} 1.4507; d_4^{20} 0.9120.

Dimethylallyl(n-butenyl)silane (XIII). To a solution of the Grignard reagent, prepared from 12 g (0.5 g-atom) of Mg and 50 g (0.336 mole) of (XII) in 250 ml of ether, at 25° was added 57.4 g (0.75 mole) of AC. The mixture was refluxed for 2 h, then the ether was distilled off, another 38.2 g of AC in 100 ml of THF was added, and the mixture was refluxed for another 2 h. Then the mixture was cooled and decomposed with water and 5% HCl solution. After the usual workup and fractional distillation we isolated 36.5 g (70%) of (XIII) with bp 163-165°, n_D^{20} 1.4436; d_4^{20} 0.7748 (cf. [10]).

1,1-Diallyl-1-silacyclobutane (IV). To the Grignard reagent (from 15 g (0.625 g-atom) of Mg and 50 g (0.65 mole) of AC in 200 ml of THF) at 40° was added 28.2 g (0.2 mole) of 1,1-dichloro-1-silacyclobutane in an equal volume of THF. The mixture was heated for 1 h at 60°, cooled, and decomposed with water and NH_4Cl solution. After the usual workup we obtained 23 g of crude product with bp 57-60° (10 mm). After chromatography on a column packed with neutral Al_2O_3 (II activity, eluant = n-hexane) and vacuum-distillation we obtained 17.5 g (57.5%) of (IV) with bp 66.5-68° (11 mm); purity ∿99.8%; n_D^{20} 1.4830 d_4^{20} 0.8496. Mass spectrum (m/z): 152 $[M]^+$, 124 $[M—C_2H_4]^+$ and (111) $[M-(CH_2=CH—CH_2)]^+$. Infrared spectrum (ν, cm^{-1}): 935, 1125, and 1195 (silacyclobutane ring), 1640 $(\rangle C=C\langle)$. PMR spectrum (δ, ppm, 30% C_6H_6 solution): 1.03 m (4H, α-CH_2 of ring), 2.07 m (2H, β-CH_2 of ring), 5.43-6.13 m (2H, CH=C), 4.8-4.98 m (4H, $=CH_2$). ^{13}C NMR spectrum (δ, ppm): 12.2 (α-C), 18.2 (β-C), 22.7 (C*C=C), 133.5 ($C^*=CH_2$), 114.0 ($C=C^*H_2$). ^{29}Si NMR spectrum: 17.1 ppm.

1,1-Dimethyl-1-sila-3-cyclopentene (II). To a solution of CH_3MgI [from 20 g (0.83 g-atom) of Mg and 85.2 g (0.6 mole) of MeI in ether] at 25° was added a solution of 30.6 g (0.2 mole) of 1,1-dichloro-1-sila-3-cyclopentene* (bp 135-136.5°; n_D^{20} 1.4780; d_4^{20} 1.2190) in an equal volume of ether. The reaction mass was refluxed for 2 h, cooled, and decomposed with water and NH_4Cl solution. After the usual workup the solvent was removed and the residue was fractionally distilled, collecting the fraction with bp 100.5-103°, which was chromatographed on a column packed with neutral Al_2O_3 (II activity, eluant = n-pentane). Fractional distillation of the eluate gave 15.2 g (68%) of (II) with bp 101.5°; n_D^{20} 1.4424; d_4^{20} 0.8062.

Aluminum—Rhenium Catalyst Re_2O_7/Al_2O_3. The γ-Al_2O_3 (surface area 180 m^2/g, 0.5-1.0 mm fraction) was ignited at 400-450° for 2 h in an air stream and for 2 h in an argon stream. Then 10 g of the Al_2O_3 was covered with a chilled solution of 2.6 g of NH_4ReO_4, prepared by dissolving in 20 ml of distilled water at the boil, and the mixture was left standing for 1 day. The obtained catalyst was dried for 2 h at 120°. Immediately before experiment the catalyst was activated for 1 h at 580° in an air stream, and then for 1 h in an argon stream.

Aluminum—Rhenium Catalyst, Promoted with $SnBu_4$. A solution of 0.03 ml of $SnBu_4$ in 3 ml of abs. pentane was added from a syringe, in an argon stream, to a receiver containing 1 g of the activated catalyst. After evaporating the solvent the receiver was hermetically sealed.

The metathesis of the dialkenylsilanes in the liquid phase on Al—Re catalyst was run in a thermostatted reactor equipped with a magnetic stirrer, a dropping funnel, and a condenser, which was connected to a gas buret for collecting the formed ethylene. The catalyst (1 g), activated before experiment, was charged in an argon stream into the reactor. Then a heptane solution of 0.01 mole of the dialkenylsilane was added. The formed ethylene was collected in the gas buret and its volume was recorded. At the end of experiment the reactor was cooled, the liquid products were decanted, the catalyst was washed thrice with the solvent, and the products were analyzed.

4,9-Disila-4,4,9,9-tetramethyl-1,6,11-dodecatriene (IIIa). The same as described above, a solution of 5.6 g (0.04 mole) of (I) in 7 ml of n-heptane was subjected to metathesis in the presence of 5 g of Re_2O_7/Al_2O_3—$SnBu_4$. Based on the chromatographic mass spectrometry data the final mixture contained 8% of (II) and 69% of (IIIa) and (IIIb). Fractional distillation gave 2.5 g (56% yield) of (IIIa), bp 129° (1 mm) $n_D^{21.5}$ 1.4729. PMR spectrum (δ, ppm): 0.05 s (12H, $SiCH_3$), 1.43 t (8H, $SiCH_2$), 4.7-4.2 t (4H, $=CH_2$), 5.0-6.1 m (4H, CH=).

Polymerization of 1,1-Dimethyl-1-sila-3-cyclopentene (II). The same as before, the polymerization of 3.4 g (0.03 mole) of (II) in 4.3 ml of n-heptane was run in the presence of 3 g of Re_2O_7/Al_2O_3—$SnBu_4$. The reaction mass was filtered from the catalyst, the filtrate was poured into MeOH, and the obtained solid polymer was dissolved in n-heptane, reprecipitated with MeOH, and dried in vacuo (10^{-2} mm) to give 1.2 g (35%) of polymer. PMR spectrum (δ, ppm): 0 s (6H, $SiCH_3$), 1.42 d (4H, $SiCH_2$), 5.22 t (2H, CH=).

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*Supplied by N. G. Komalenkova.

Metathesis of Diallylsilacyclobutane (IV). In a similar manner, the metathesis of a solution of 4.6 g (0.03 mole) of (IV) in 4.3 ml of n-heptane was run in the presence of 3 g of Re_2O_7/Al_2O_3—$SnBu_4$. The catalyzate was filtered and distilled. Analysis by chromatographic mass spectrometry disclosed that the distillate contains 5% of (V) and 25% of (VI). The residue represented a waxy polymeric product (∿35%). Mass spectrum of (V), m/z (intensity, %): 53(7), 55(17), 67(7), 68(12), 69(5), 70(10), 81(8), 82(25), 83(8), 95(13), 96 $[M-C_2H_4]^+$, 97(10), 124 (M^+, 30).

The chromatographic mass spectrometric analysis was run on an LKV-2091 instrument (temperature of ionization chamber and molecular separator = 250°, ionization energy = 70 eV, and emission current = 50 μA) using a 70×0.25 mm capillary column packed with Apiezon L. The PMR spectra were taken on a Varian T-60 instrument (60 MHz) using CCl_4 as the solvent and TMS as the standard, the ^{13}C NMR spectra were taken on a Bruker VP-80 instrument (20.115 MHz), and the IR spectra were taken on a UR-20 instrument.

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CONCLUSIONS

1. It was shown that the efficient metathesis of dialkenylsilanes of variable structure in the presence of aluminum—rhenium catalysts is possible.

2. Conditions were found for the preparative synthesis of 4,9-disila-4,4,9,9-tetramethyl-1,6,11-dodecatriene and 1,1-dimethyl-1-sila-3-cyclohexene via the inter- and intramolecular metathesis reaction.

3. 1,1-Dimethyl-1-sila-3-cyclopentene polymerizes to a linear polysilapentenomer in the presence of Al—Re catalysts.

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