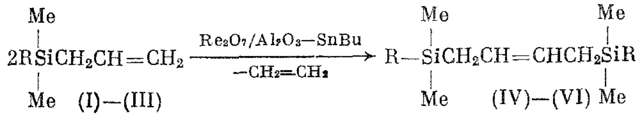
METATHESIS OF ALLYLSILANES WITH AROMATIC SUBSTITUENTS

V. M. Vdovin, N. V. Ushakov,
E. B. Portnykh, E. Sh. Finkel'shtein,
and N. P. Abashkina

UDC 542.91:547.1'128

The present work is devoted to a study of the metathesis of alkenyl derivatives of Group IVB elements. In previous work [1], we showed that, upon contact with an alumorhenium catalyst promoted by $SnBu_4$, dialkenylsilanes with methyl substituents vigorously eliminate ethylene to form cyclic and linear products of intra- and intermolecular metathesis, respectively. In a study of the range of application of this reaction, we subjected allylsilanes containing aromatic substituents to metathesis on $Re_2O_7/Al_2O_3-SnBu_4$. Neither the Si—Ar group ($Si-C_{sp^2}$ bond) nor the $Si-CH_2-Ar$ group ($Si-C_{sp^3}$ bond) hinders the metathesis. In all the cases studied, the corresponding 1,4-bis(aryldimethylsilyl)-2-butenes or 1,4-bis(benzyldimethylsilyl)-2-butenes were formed



$$2R\underset{Me}{\overset{Me}{Si}}CH_2CH=CH_2 \xrightarrow[-CH_2=CH_2]{Re_2O_7/Al_2O_3-SnBu} R-\underset{Me}{\overset{Me}{Si}}CH_2CH=CHCH_2\underset{Me}{\overset{Me}{Si}}R$$

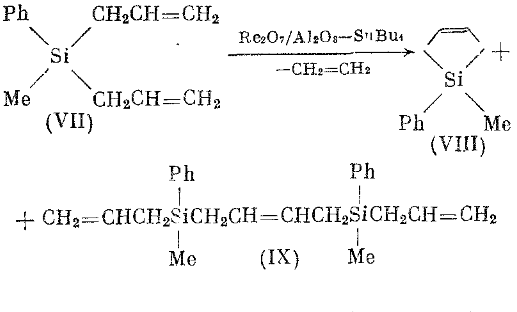
(I)—(III) (IV)—(VI)

R = Ph (I), (IV), *p*-Tol (II), (V), Bz (III), (VI).

In this case, (II), in which the Si—Ar bond should be more sensitive to acid action than in (I) [2], does not show a significant relative decrease in activity: the yield of (IV) is 50-60% and the yield of (V) is 45-55%, while (VI) is formed in even higher yields (65-75%).

We should note that another alkenylsilane, trimethylvinylsilane, which, similar to arylsilanes, has an sp^2-hybridized carbon atom bound to the silicon atom, has significantly less activity (the conversion of $Me_3Si-CH=CH_2$ under analogous conditions is only 5-7%). Apparently, there is inhibition in this case due to the formation of a stable carbene complex, $Me_3SiCH{:}Re$, which is in accord with the data of Dolgoplosk et al. [3] on the inhibiting effect of $Me_3Si-CH=CH_2$ on olefin metathesis in the presence of the $(RO)_2WCl_4-EtAlCl_2$ system.

Phenylmethyldiallylsilane (VII), similar to diallylsilanes with methyl groups [1], undergoes metathesis both by intra- and intermolecular pathways



to form 1-phenyl-1-methyl-1-sila-3-cyclopentene (VIII) (10-15% yield) and 4,9-diphenyl-4,9-dimethyl-4,9-disila-1,6,11-dodecatriene (IX) (50-60% yield), respectively. Distillation permitted isolation of a sample of (VIII) with 93% purity (as indicated by gas—liquid chromatography). Its mass spectrum shows an ion with m/z corresponding to the loss of butadiene, which is characteristic for sila-3-cyclopentenes, in addition to a strong molecular ion and an ion corresponding to loss of a CH_3 group [1]. The most intense ion peak corresponds to

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A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2121-2123, September, 1984. Original article submitted November 4, 1983.

the simultaneous loss of butadiene and a CH_3 radical. As expected, the molecular ion in the mass spectrum of (IX) is not pronounced (1% intensity), but the $[M - allyl]^+$ ion is present. The peak with maximum intensity corresponds to the ion fragment formed in the cleavage of the bridging $Si-C_{allyl}$ bond, which is also characteristic for 4,4,9,9-tetramethyl-4,9-disila-1,6,11-dodecatriene [1].

Products (IV)-(VI) were separated and characterized. Their structures were supported by PMR and mass spectroscopy. The elemental analysis data were also in accord with the structures assigned.

EXPERIMENTAL

The chromato-mass spectral analysis was carried out on an LKB-2091 spectrometer on an SE-30 column. The PMR spectra were taken on a Varian T-60 spectrometer in CCl_4 solution relative to TMS as internal standard.

Phenyldimethylallylsilane (I) was prepared by the allylation of phenyldimethylchlorosilane in 45% yield, bp 87-89°C (4 mm), n_D^{20} 1.5084 [4]. PMR spectrum (δ, ppm): 0.21 s (6H, CH_3Si), 1.63 m (2H, $SiCH_2C{=}$), 4.72 m (2H, $CH_2{=}$), 5.64 m (1H, $CH{=}$), 7.0-7.46 m (5H, arom.).

p-Tolyldimethylallylsilane (II) was prepared by allylation of p-tolyldimethylchlorosilane in 56% yield, bp 94-96°C (5 mm), n_D^{20} 1.5079 [5]. PMR spectrum (δ, ppm): 0.25 s (6H, CH_3Si), 1.71 m (2H, $SiCH_2C{=}$), 2.33 s (3H, CH_3Ar), 4.84 m (2H, $CH_2{=}$), 5.77 m (1H, $CH{=}$), 6.96-7.48 m (4H, arom.).

Benzyldimethylallylsilane (III) was prepared by the allylation of benzyldimethylchlorosilane in 45% yield, bp 110-114°C (18-20 mm), n_D^{22} 1.5095 [5]. PMR spectrum (δ, ppm); 0.01 s (6H, CH_3Si), 1.51 m (2H, $SiCH_2C{=}$), 2.07 s (2H, $SiCH_2Ar$), 4.8 m (2H, $CH_2{=}$), 5.62 m (1H, $CH{=}$), 6.7-7.2 m (5H, arom.).

Phenylmethyldiallylsilane (VII) was prepared by the allylation of phenylmethyldichlorosilane in 54% yield, bp 80-82°C (1.8 mm), n_D^{20} 1.5223 [6]. PMR spectrum (δ, ppm): 0.25 s (3H, CH_3Si), 1.72 m (4H, $SiCH_2C{=}$), 4.76 m (4H, $CH_2{=}$), 5.67 m (2H, $CH{=}$), 7.23 m (5H, arom.).

Metathesis of Phenylmethyldiallylsilane (VII). A mixture of 1 g $Re_2O_7/Al_2O_3-SnBu_4$ catalyst prepared according to our previous work [1] and a solution of 2.02 g (0.01 mole) (VII) in 15 ml heptane was stirred at 45°C. Upon completion of the liberation of ethylene, the reaction mixture was filtered and analyzed by chromato-mass spectroscopy. The yield of (VIII) was 13%, while the yield of (IX) was 56%. Distillation gave 0.12 g (VIII) with 93% purity (as indicated by gas–liquid chromatography, bp 73-77°C (4.5-5 mm) [7]. Mass spectrum of 1-phenyl-1-methyl-1-sila-3-cyclopentene (VIII), m/z (rel. intensity, %): 174 $[M]^+$ (68), 159 $[M - CH_3]^+$ (90), 146(16), 145(7.5), 131(14), 129(4), 120$[M - C_4H_6]^+$ (50), 105 $[M - C_4H_6 - CH_3]^+$ (100), 103(3), 96(37), 95(5), 93(5), 79(17), 77(3), 73(4), 55(5), 54(3), 53(23), 51(3). Mass spectrum of 4,9-diphenyl-4,9-dimethyl-4,9-disila-1,6,11-dodecatriene (IX), m/z (%): 376 $[M]^+$ (1.0), 335$[M - C_3H_5]^+$ (15), 307(5), 257(16), 229(2.5), 197(18), 161$[AllSi(Ph)Me]^+$ (100), 159(14), 147(2), 146(2.2), 145(8.5), 135(19.5), 133(4.7), 131(3.7), 121(38), 119(3.2), 107 (5.5), 106(2), 105(13), 96(3.2), 95(2.2), 91(2.7), 53(2).

1,4-Bis(phenyldimethylsilyl)-2-butene (IV). The method described above was used to carry out the metathesis of 8.8 g (0.05 mole) (I) on 5.5 g $Re_2O_7/Al_2O_3-SnBu_4$ in 10 ml heptane. The yield of (IV) was 54% as indicated by gas–liquid chromatography. After filtration, washing of the catalyst, and removal of the solvent, the residue was distilled in vacuum. The yield of pure (IV) was 35%, bp 106-110°C (0.07-0.08 mm), n_D^{20} 1.5396. PMR spectrum (δ, ppm): 0.18 s (12H, CH_3Si), 1.5 m (4H, $SiCH_2C{=}$), 5.2 m (2H, $CH{=}CH$), 7.23 m (10H, arom.). Mass spectrum, m/z (%): 324 $[M]^+$ (4), 197(2.5), 174(5.6), 159(3.2), 135 $[PhSiMe_2]^+$ (100), 119(3) , 112(7), 107(7.3), 105(8), 97(2), 96(3.7), 95(10), 43(9.7).

1,4-Bis(p-tolyldimethylsilyl)-2-butene (V). An analogous procedure was used for the metathesis of 9.5 g (0.05 mole) (II) on 5.5 g $Re_2O_7/Al_2O_3-SnBu_4$ in 10 ml heptane. After the usual work-up, the yield of (V) was 63%, as indicated by gas–liquid chromatography, and 33% after vacuum distillation, bp 155-158°C (0.7 mm), n_D^{20} 1.5356. PMR spectrum (δ, ppm): 0.18 s (12H, CH_3Si), 1.57 m (4H, $SiCH_2C{=}$), 2.33 s (6H, CH_3Ar), 5.21 m (2H, $CH{=}CH$), 7.15 m (8H, arom.).

1,4-Bis(benzyldimethylsilyl)-2-butene (VI). A similar metathesis was carried out for 9.5 g (0.05 mole) (III) on 5.5 g $Re_2O_7/Al_2O_3-SnBu_4$. The yield of (VI) was 70%, as indicated by gas–liquid chromatography, and 41.5% after vacuum distillation, bp 150-153°C (0.6-0.8 mm),

n_D^{20} 1.5410, d_4^{20} 0.9514. PMR spectrum (δ, ppm): 0.03 s (12H, CH_3Si), 1.41 m (4H, $SiCH_2C{=}$), 2.11 s (4H, $SiCH_2Ar$), 5.27 m (2H, CH=CH), 6.8-7.25 m (10H, arom.). Mass spectrum, m/z (%): 352 $[M]^+$ (6.0), 261 $[M - C_6H_6CH_2]^+$ (2), 173(2), 149 $[BzSiMe_2]^+$ (100), 121(25), 97(6), 91(2), 73(10), 59(2), 45(5), 43(5).

CONCLUSIONS

The feasibility was demonstrated for the efficient metathesis of phenyltolyl- and benzylallylsilanes on an alumorhenium catalyst promoted by tetrabutyltin. The metathesis of aryldimethylallylsilanes or aralkyldimethylallylsilanes is a preparative method for the synthesis of 1,4-bis(aryldimethylsilyl)-2-butenes or 1,4-bis(aralkyldimethylsilyl)-2-butenes.

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HYDRATION OF PHENYLACETYLENE IN FORMIC ACID

M. G. Voronkov, G. Yu. Zhila,
and N. N. Vlasova

UDC 542.934:547.538.241

The hydration of acetylenic compounds, including phenylacetylene, is accomplished at high temperature and in the presence of acid catalysts such as mineral acids, mercury oxides and salts, and $Et_2O{\cdot}BF_3$ [1-3].

In a study of the photochemical hydration of phenylacetylene (I) in the presence of HCO_2H, we discovered its conversion to acetophenone (II)

$$PhC{\equiv}CH \xrightarrow{H_2O} PhCOMe$$

The addition of water to (I) is accomplished most efficiently in HCO_2H containing 10 mole % water: the yield of (II) is 46% after 3.5 h and 68% after 8 h. The observed hydration is not a photochemical process, but rather occurs in the dark and involves the usual electrophilic mechanism. However, radiation accelerates this reaction. Thus, the yield of (II) upon UV irradiation using a DRT-400 lamp at a distance of 8-10 cm from the reaction vessel is 40% after 3.5 h relative to a yield of only 7% for the same time period in the dark at 60-70°C. This irradiation effect is apparently a result of the hydration of (I) due to the water formed together with CO from HCO_2H as a result of photodissociation. This proposal is supported by the observed formation of (II) upon the irradiation of a mixture of (I) and anhydrous formic acid.

EXPERIMENTAL

The reaction course was monitored by gas—liquid chromatography on an LKhM-8M chromatograph on a 1-m SE-30 column with helium gas carrier and an authentic sample of (II). The purity of the sample of (II) obtained was indicated by PMR spectroscopy on a Tesla BS-487 spectrometer at 80 MHz with HMDS internal standard: δ_{CH_3CO} 2.41 ppm, $\delta_{C_6H_5}$ 7.89 and 7.40 ppm, and elemental analysis data.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2123-2124, September, 1984. Original article submitted November 9, 1983.

0568-5230/84/3309-1939$08.50