STEREOSELECTIVITY OF HYDROSILYLATION OF OLEFINS

UDC 542.91:541.634:547.1'128

A. V. Podol'skii, T. G. Cherezova, V. P. Kachalkov, and M. I. Kodess

We used the procedure described in [2] to study the stereoselectivity of hydrosilylation (HS) in the presence of H_2PtCl_6 [1-3] by comparing the reactivity of the cis and trans isomers of propenylbenzene, 1-propenylnaphthalene, and stilbene when reacted with hydrosilanes MeR_2SiH, where $R = C_5H_{11}(I)$, Ph(II), PhCH₂(III). The HS of the trans isomers of propenylbenzene and stilbene using chlorosilanes was described in [4, 5].

Initially the cis-propenylbenzene is converted to the cis-isomer and the hydrosilane is not consumed. HS begins when the amount of trans-propenylbenzene reaches a certain value. The HS rate does not decrease as the cis isomer is consumed (Fig. 1). The HS of the pure trans-propenylbenzene is not accompanied by isomerization and goes somewhat more rapidly than the HS of the cis isomer. A study of the competing HS of a mixture of the cis and trans isomers of 1-propenylnaphthalene disclosed that only the trans isomer reacts under the found conditions (Table 1). Based on the GLC analysis, alkylaromatic compounds are not formed during the HS of the propenylbenzenes and 1-propenylnaphthalenes. More drastic conditions, which cause side reactions, are required for the HS of the stilbenes. However, also here the cis-stilbene is initially isomerized to trans-stilbene, while trans-stilbene reacts slowly under the same conditions without isomerization. Special experiments disclosed that the cis-olefins isomerize only in the common presence of hydrosilane and H_2PtCl_6 .

Within the framework of the HS mechanism discussed in [6], the observed facts can be explained by the following scheme:



TABLE 1. Reaction Conditions and Conversion during Hydrosilylation of Olefins

Olefin	Hydro- silane	т., ℃	$[H_2PtCl_6] \cdot 10^5$, mole /mole of silane	Timę, min	Conversion, of	
					based on olefin	based on hydrosilane
cis-Propeny Ibenzene	(I)	80	8 16 48	100 30 30	25 * 30 * 55 *	0 0 12
trans-Propeny lbenzene	(I) (II)	80 80	48 48	210 210	35 28	29 24
Mixture of cis- and trans- 1- propeny inaphthalenes	(I) (II)	150 150	8 24 48	240 120 225	27 † 47 † 29 †	32 54 35
cis-Stilbene	(111)	200	100	180 300	79 * 86 *	0 14
trans-Stilbene	(III)	200	100	300 660	11 26	20 66
*Conversion of cis isomer to trans isomer.						

+Consumption of trans isomer.

Institute of Chemistry, Ural Scientific Center of the Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 215-217, January, 1979. Original article submitted May 23, 1978.



Fig. 1. Kinetic curves for consumption of reactants during HS of cis-propenylbenzene using hydrosilanes (I) (1, 3, 5) and (II) (2, 4, 6) at 80°C and $[H_2-$ PtCl₆] = 4.8 10⁻⁴ mole/mole of silane: 1) (I); 2) (II); 3, 5) cis-propenylbenzene; 4, 6) trans-propenylbenzene; C_{re} = reduced concentration based on [8].

The cis-isomers rapidly form the π complex K_{π}^{cis} . The K_{π}^{cis} , probably due to steric factors, cannot change to the σ complex K_{σ} , which is responsible for the HS, and instead dissociates into the starting reactants, with the simultaneous conversion of the cis isomer to the trans isomer. The latter accumulates, since it forms a less stable π complex than the cis isomer [7]. The K_{π}^{trans} complex is formed as the cis isomer is consumed and the trans isomer accumulates, which then changes to K_{σ} by the trans-addition mechanism Pt-H to the coordinated olefin.

EXPERIMENTAL

The HS was studied by the GLC method using phenylcyclohexane as the internal standard and an equimolar ratio of the reactants. A double amount of the hydrosilane was used in the case of stilbene.

The GLC analysis was run on a UKh-2 instrument, which was equipped with a 2 m \times 6 mm column, packed with 15% PEG 40 M deposited on Chromaton N-AW-HMDS. At 226° and a helium flow rate of 9 liters/h the exit time for cis-1-propenylnaphthalene, 1-allylnaphthalene, trans-1-propenylnaphthalene, cis-stilbene, and trans-stilbene was respectively 4.1, 5.4, 5.9, 5.5, and 13.1 min. The exit time for allylbenzene, and cis- and trans-propenylbenzene at 173° and a helium flow rate of 3.3 liters/h was respectively 90, 103, and 120 sec. The PMR spectra were recorded on an NR-2305 instrument (60 MHz).

The synthesis of hydrosilanes (I)-(III) and the method used to plot the kinetic curves are described in [8]. trans-Propenylbenzene was obtained by the isomerization of allylbenzene on Al₂O₃ [9]: bp 177°, n_D^{20} 1.5468, cf. [10]. cis-Propenylbenzene was synthesized by the following scheme:



The yield was 46%, and the constants were bp 56.5° (10 torr) and nD^{20} 1.5385, cf. [10]. In harmony with [9], the isomerization of 1-allylnaphthalene gave a mixture of cis- and trans-1-propenylnaphthalenes in a 2:3 ratio (based on the GLC data), from which the trans-1-propenylnaphthalene was isolated: bp 139° (11 torr), nD^{20} 1.6378. PMR spectrum (CC1₄, δ , ppm, internal standard TMS, ABX₃ system): 1.8 (CH₃), 6.0 (Me-CH=), 7.0 (Ar-CH=); Jtrans-CH=CH-= 16, JMe-H=6.5 and 1.6 Hz. Infrared spectrum (ν , cm⁻¹): 968 (trans-CH=CH-). "Scintillation" trans-stilbene was used as such. cis-Stilbene was obtained by the decarboxylation of trans- α -phenylcinnamic acid on BaO; bp 138-139° (10 torr), nD^{20} 1.6209, cf. [11].

CONCLUSIONS

It was discovered that disubstituted olefins, in which the double bond is conjugated with an aromatic system, exhibit stereoselective hydrosilylation: only the trans isomers react directly. The hydrosilylation of the cis isomers is accomplished via prior conversion to the trans isomers. It was postulated that the stereoselectivity of the process is based on the trans-addition mechanism.

LITERATURE CITED

- 1. R. A. Benkeser, Pure Appl. Chem., 13, 133 (1966).
- 2. M. Capka, P. Svoboda, V. Bazant, and V. Chvalovsky, Chem. Prumysl, 21, 324 (1971).
- 3. J. V. Swisher and C. Zullig, J. Org. Chem., <u>38</u>, 3353 (1973).
- 4. M. C. Musolf and J. L. Speier, J. Org. Chem., 29, 2519 (1964).
- 5. A. I. Nogaideli, L. I. Nakaidze, and V. S. Tskhovrebashvili, Zh. Obshch. Khim., <u>44</u>, 1763 (1974).
- 6. C. S. Cundy, B. M. Kingston, and M. F. Lappert, Advances Organomet. Chem., <u>11</u>, 297 (1973).
- 7. F. Conti, L. Raimondi, G. F. Pregaglia, and R. Ugo, J. Organomet. Chem., 70, 107 (1974).
- 8. A. V. Podol'skii, T. G. Cherezova, and M. A. Bulatov, Zh. Obshch. Khim., <u>47</u>, 1527 (1977).
- 9. R. Ya. Levina, L. E. Karelova, and I. A. El'yashberg, Zh. Obshch. Khim., 10, 913 (1940).
- 10. R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, J. Am. Chem. Soc., <u>75</u>, 4094 (1953).
- 11. G. Wittig and W. Haag, Chem. Ber., 88, 1654 (1955).

MASS SPECTROMETRIC STUDY OF ALKENYL-,

ALKADIENYL-, AND CYCLOALKENYLSILANES

V. N. Bochkarev, E. G. Galkin,

UDC 543.51:547.1'128

I. M. Salimgareeva, and E. M. Vyrypaev

The hydrosilylation of conjugated polyenes is a convenient method for the synthesis of various compounds with an unsaturated substituent on the Si atom [1]. It is expedient to identify the obtained compounds employing mass spectrometry, but the existing literature data on the decomposition of alkenylsilanes under electron impact (EI) are very scanty [2-4]. In order to establish the general paths for the fragmentation of unsaturated silanes and the contribution made by the various paths as a function of the nature of the substituents on the Si atom, and also as a function of the number and mutual arrangement of the multiple bonds in a hydrocarbon substituent, we studied the mass spectra of alkenyltrialkylsilanes (Ia)-(Ie), alkadienyltrialkylsilanes with unconjugated (If)-(Ii) and conjugated bonds (II), alkenyldimethylsilane (IIIa), alkadienyldimethylsilane (IIIb), alkenylphenylsilanes (IIIc, d), alkadienylphenylsilane (IIIe), alkenylethoxysilane (IIIf), and silanes (IV) and (V), which contain cycloalkenyl substituents. For comparison we also studied the spectrum of (2-methylbutyl)triethylsilane (VI).

XCH₂CH=CYCHZSiR₃ CH₂=CHCH=CH₂CH₂SiMe₃ XCH₂CH=CYCH₂SiHRR' (III) (II) (1) X = Y = H, R = R' = Me (IIIa); X = Y = Z = H, R = Me (Ia); $X = CH_3CH = CHCH_2, Y = H,$ X = D, Y = Z = H, R = Me (Jb); R = R' = Me (III b); X = Y = R' = H, R = Ph (III c); X = Y = H, Z = R = Me (Ic); $\mathbf{X} = \mathbf{M}\mathbf{e}, \ \mathbf{Y} = \mathbf{R'} = \mathbf{H},$ X = Y = Z = H, R = Et (Id); R = Ph (III d): $X = CH_3CH = CHCH_2,$ X = Z = H, Y = Me, R = Et (Ie); Y = R' = H, R = Ph (IIIe);

Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 217-221, January, 1979. Original article submitted May 15, 1978.

203