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DIFFERENTIATION OF GEOMETRIC ISOMERS OF TRISUBSTITUTED VINYLSILANES BY NMR AND GLC

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There has recently been considerable interest in the use of vinylsilanes as synthetic intermediates.[1] In our opinion, vinylsilanes will serve as important precursors for the stereospecific synthesis of substituted alkenes[2,4] because the silyl group can be replaced with ease by electrophiles such as proton[5], halogens[6] or carbocations[7] with apparently high stereospecificity.[8,9] Of particular interest is the possible use of this approach for the stereospecific synthesis of trisubstituted alkenes because of their wide-spread occurrence in nature. The development[2-4] of the stereospecific synthesis of trisubstituted vinylsilanes from readily available starting materials has enhanced the prospect of such an approach.

In the course of our investigation, it became necessary to find a facile method for the differentiation of geometric isomers of trisubstituted vinylsilanes. The usual approach is to convert the isomeric vinylsilanes by protodesilylation to the disubstituted alkenes.[2,4] The assignment of stereochemistry is predicated then on (a) the stereochemistry of the product alkene can be determined with ease and (b) the substitution of silyl group by proton proceeds with retention of configuration. We report here an alternative method based on the difference of ^{1}H and ^{13}C nmr spectra as well as GLC retention times.

Proton nmr Spectra of Vinylsilanes

The chemical shifts of vinyl protons can be predicted reasonably well according to the empirical equation, $\delta C{=}C{-}H{=}5.25{+}\Sigma Z$ where the Z-factors are the substituent shielding coefficients.[10] Unfortunately, the Z-values for the trimethylsilyl group have not been determined.[11] In Table 1, we have collected the chemical shifts of the vinyl protons as well as the methyl protons of the trimethylsilyl group for a number of isomeric trisubstituted vinylsilanes. In all cases, the chemical shifts of the vinyl protons for the E-isomers are consistently about 0.3 ppm higher field than the corresponding Z-isomers. Using only measurements from our laboratories, (Table 1, entries 1-4, 9-12) for the sake of consistency, we obtained $Z_{cis} = 0.11$ and $Z_{trans} = 0.35$ for the trimethylsilyl group. The chemical shifts of the methyl protons of the trimethylsilyl group of the E-isomers are also at a higher field than that of the Z-isomers. The difference is however small (∿0.08 ppm) and may not be reliable enough for structural diagnosis. Nevertheless, they are useful for the quantitative determination of the relative proportions of the isomers in a given mixture.

^{13}C nmr Spectra of Vinylsilanes

We have examined the ^{13}C nmr of a number of isomeric trisubstituted vinylsilanes. In

Table 1. NMR Data of Vinylsilanes $Me_3Si-C(R)=CHR^1$

Vinylsilanes	Stereo-chemistry	^1H-NMR(CCl_4), δ [ppm]		^{13}C-NMR($CDCl_3$), δ [ppm]		
		C=C-H	$\underline{CH_3}$-Si	$\underline{CH_3}$-Si	=$\underline{C}$-Si	=$\underline{C}$-H
1. $R=C_2H_5$, $R^1=c\text{-}C_6H_{11}$	E	5.52	0.05	-1.08	140.05	145.87
	Z	5.71	0.13	0.56	138.79	147.81
2. $R=n\text{-}C_5H_{11}$, $R^1=i\text{-}C_3H_7$	E	5.51	0.05	-1.035	137.89	147.68
	Z	5.80	0.13	0.604	136.29	150.40
3. $R=n\text{-}C_5H_{11}$, $R^1=n\text{-}C_{10}H_{21}$	E	5.53	0.05	-1.035	140.90	140.47
	Z	5.83	0.13	0.431	139.18	143.11
4. $R=(CH_2)_4-CH(CH_3)_2$, $R^1=n\text{-}C_{10}H_{21}$	E	5.53	0.05	-1.035	140.86	140.43
	Z	5.83	0.13	0.431	139.25	143.15
5.[a] $R=CH_3$, $R^1=n\text{-}C_6H_{13}$	E	5.63	0.03			
	Z	5.92	0.10			
6.[a] $R=CH_2-CH=CH_2$, $R^1=n\text{-}C_6H_{13}$	Z	5.97	0.12			
7.[a] $R=CH_2-C(CH_3)=CH_2$, $R^1=n\text{-}C_6H_{13}$	Z	5.90	0.10			
8.[a] $R=CH_2-C(Cl)=CH_2$, $R^1=n\text{-}C_6H_{13}$	Z	5.99	0.14			
9.[c] $R=CH_2Cl$, $R^1=i\text{-}C_3H_7$	E	5.78	0.14			
	Z	6.08	0.22			
10.[c] $R=CH_2Cl$, $R^1=c\text{-}C_6H_{11}$	E	5.78	0.14			
	Z	6.08	0.22			
11.[b] $R=CH_2Cl$, $R^1=t\text{-}Bu$	E	5.75	0.15			
	Z	6.35	0.30			
12.[c] $R=CH_2Cl$, $R^1=n\text{-}C_{10}H_{21}$	Z	6.28	0.22			

(a). Data obtained from reference (4). (b) Data obtained from T.H. Chan, B.S. Ong and W. Mychajlowskij, Tetrahedron Letters, 3253 (1976). (c) T.H. Chan, W. Mychajlowskij, B.S. Ong and D.N. Harpp, J. Organomet. Chem., 107, C-1 (1976).

all cases, the methyl carbons of the trimethylsilyl groups of the E isomers resonate at a higher field than that of the Z isomers (Table 1). The difference is large (∿1.5 ppm) and consistent enough to be useful as a method for structural differentiation. The use of the ^{13}C chemical shift for stereochemical assignment of di- and trisubstituted alkenes has been recognised.[12] They are based typically on the observation that the α-carbons which have more steric interactions are more shielded.[13] The reverse is apparently true in the present case. The trimethylsilyl carbons which are more sterically encumbered (the Z isomer) are less shielded. We attributed this to the so-called δ effect[14], i.e., a 1,5(δ) CH_3-CH_3 relationship may lead to a downfield shift when these groups are suitably oriented with respect to each other.[13]

Gas Liquid Chromatography (GLC) of Vinylsilanes

Whereas the analysis of organosilicon compounds by GLC has been examined quite extensively,[15] the study of geometric isomers of vinylsilanes has not been reported to our knowledge. We have submitted four pairs of isomeric trisubstituted vinylsilanes to GLC analysis. The ratio of retention time of the Z isomer relative to the E isomer is greater than unity (Table 2) in all cases. While this observation is consistent with those obtained for isomeric alkenes, caution must be exercised in using this information alone for stereochemical assignment.[16]

In conclusion, we feel that nmr, in conjunction with GLC, can be applied profitably to the qualitative as well as the quantitative determination of geometric isomers of trisubstituted vinylsilanes.

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Table 2: GLC data of Vinylsilanes $Me_3Si{-}C(R){=}CHR^1$

VINYLSILANES	$t_RZ:t_RE$ (column temperature)			
	COLUMN I	COLUMN II	COLUMN III	COLUMN IV
1. $R = C_2H_5$, $R^1 = c\text{-}C_6H_{11}$	1.06(135°)	1.05(210°)	1.06(110°)	1.00(130°)
2. $R = n\text{-}C_5H_{11}$, $R^1 = i\text{-}C_3H_7$	1.25(125°)	1.20(190°)	1.19(90°)	1.13(120°)
3. $R = n\text{-}C_5H_{11}$, $R^1 = n\text{-}C_{10}H_{21}$	1.16(200°)	1.14(300°)	1.16(180°)	1.13(210°)
4. $R = (CH_2)_4\text{-}CH(CH_3)_2$, $R^1 = n\text{-}C_{10}H_{21}$	1.17(220°)	1.16(300°)	1.15(190°)	1.11(210°)

t_R = retention time

Column I: 12', 1/8";20% carbowax 20M on chromosorb W-AW-DMCS (60/80 mesh) - Carrier Gas Flow (helium) = 50 ml/min.

Column II: 20', 1/8"; 20% Apiezon L on chromosorb W-AW-SMCS (60/80 mesh); Helium Flow = 40 ml/min.

Column III: 20', 1/8"; 10% Diethyleneglycolsuccinate on chromosorb W-AW-DMCS (80/100 mesh);Helium Flow = 30 ml/min.

Column IV: 6', 1/8"; 10% SE 30 on chromosorb W-AW-DMCS (80/100 mesh); Helium Flow = 40 ml/min.