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Analysis of spectral parameters of *trans*- and *cis*-silyl substituted 1,2-dihalogenoethenes including one-bond CC spin–spin coupling constants across double bonds

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Abstract

Some *trans*- and *cis*-1-trialkylsilyl-1,2-dihalogenoethenes have been synthesized and their ^{13}C and ^{1}H NMR spectra recorded. The compounds studied readily undergo reversible *cis–trans* isomerization, the *cis* isomers being thermodynamically more stable than the *trans* isomers. The value of $^{3}J(\mathrm{SiH}\alpha)_{trans}$ is about twice as large as that of $^{3}J(\mathrm{SiH}_{\alpha})_{cis}$, and the values of $^{2}J(\mathrm{C}_{\beta}\mathrm{H}_{\alpha})_{trans}$ is about one-tenth that of $^{2}J(\mathrm{C}_{\beta}\mathrm{H}_{\alpha})_{cis}$ and this allows ready assignment of the configuration. The one-bond spin–spin coupling constants between the ethylenic carbons depend on the electronegativities of the substituents, *trans* $^{1}J(\mathrm{C{=}C})$ in most cases being larger than $^{1}J(\mathrm{C{=}C})_{cis}$.

Introduction

A recent analysis of influence of substituents on spin–spin coupling constants in substituted acetylenes revealed that $^{1}J(\mathrm{C{\equiv}C})$ values depend linearly on the product of electronegativities of substituents attached to the triple bond (eq. 1) [1]. For

$$^{1}J(\mathrm{C{\equiv}C}) = 23.23E_{x} \cdot E_{y} + 15.45 \qquad (1)$$

strongly electronegative substituents, such as halogen atoms, the product on the right hand side of eq. 1 is much larger than the constant term, and so the equation can be reduced to the form:

$$^{1}J(\mathrm{C{\equiv}C}) = 23.23E_{x} \cdot E_{y} \qquad (2)$$

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The latter corresponds to the relationship proposed by Egli and von Philipsborn [2] (eq. 3), where the I_A and I_B factors are square roots of the $^1J(CC)$ values in

$$^1J(C_AC_B) = I_A \cdot I_B \qquad (3)$$

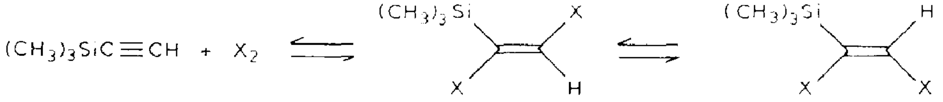
symmetrically-substituted compounds.

We thought it of interest to extend our studies to spin–spin coupling constants across CC double bonds. It might be expected that in this case the electronegativity of substituents should again be the main factor governing the $^1J(C{=}C)$ magnitude [3], and a relationship analogous to eq. 3 should hold. In the case of C=C bonds, however, steric interactions between substituents are likely to result in some deviations from the simple multiplicativity rule and, so the influence of the geometry of the compounds must also be taken into account.

Thus we decided to analyse the $^1J(C{=}C)$ values for *cis*- and *trans*-1-trialkylsilyl-1,2-dihalogenoethenes $(CH_3)_3SiCX{=}CHX$, where X = Cl, Br or I, and to compare them with the data for the corresponding dihalogenoethenes XCH=CHX X = F, Cl, Br, I. We found, however, that the question of the geometry of 1-trialkylsilyl-1,2-dihalogenoethenes, which were first synthesized almost thirty years ago [4,5], had until now been ignored. The data we have obtained provide evidence for the structures of the title compounds; this evidence is based on the measurements of dipole moments and analysis of IR and NMR spectral parameters. The $^1J(C{=}C)$ values obtained are discussed from the point of view of applicability of the multiplicative scheme and in terms of the relative stabilities of *cis* and *trans* isomers.

Results

trans-(**1a**–**1c**) and *cis*-1-trimethylsilyl-1,2-dihalogenoethenes (**2a**–**2c**) were prepared as shown in eq. 4 by addition of halogen to $(CH_3)_3SiC{\equiv}CH$.



(**1a**, X = Cl ;
1b, X = Br ;
1c, X = I)

(**2a**, X = Cl ;
2b, X = Br ;
2c, X = I)

(4)

The addition took place either under the influence of light or in the dark in the presence of catalyst. It always gave the *trans*-isomer, which subsequently isomerized into the *cis*-species. The conditions used for the synthesis and the isomerization are summarized in Table 1.

The *trans* ⇌ *cis* isomerization took place very readily in the case of 1-trimethylsilyl-1,2-dichloro- (**1a**) and 1-trimethylsilyl-1,2-dibromo-ethenes (**1b**). Pure *trans* isomers could be obtained only from reaction in the dark in the presence of a catalyst. Upon exposure to sunlight in the presence of traces of Br_2 samples of **1a** and **1b** (μ 1.2 D in the latter) were converted into the *cis* forms (μ 2.3 D in **2b**) within a few minutes. The content of the *trans*-isomer in the final mixtures as judged from GLC and NMR data was not higher than 10% for **1a** and 5% for **1b**. A similar result was obtained when a solution of pure **1b** in cyclooctane was refluxed (154 °C) in the dark with a minute amount of Br_2 for 16 h.

Table 1

Conditions used for synthesis and isomerization of *trans* (**1a**–**1c**) and *cis*-1-trimethylsilyl-1,2-dihalogenoethenes (**2a**–**2c**) $(CH_3)_3SiCX{=}CHX$ (X = Cl (**a**), Br (**b**), I (**c**), and values of the isomer ratio[a]

	Conditions	Isomer	X = Cl **a**	X = Br **b**	X = I **c**
Synthesis	catalyst in darkness	*trans*-**1**	100	100	[b]
		cis-**2**	–	–	
	hν	*trans*-**1**	–	5	100
		cis-**2**		95	–
Isomerization	*hν* + trace of Br_2	*trans*-**1**	8	5	[b]
		cis-**2**	92	95	
	boiling in cyclooctane containing catalytic amount of halogen	*trans*-**1**	n.d.	5	10
		cis-**2**	n.d.	95	90

[a] Estimated by GLC and/or NMR. [b] This could not be obtained by this method.

The conversion of *trans*-1-trimethylsilyl-1,2-diodoethene (**1c**) into its *cis*-isomer **2c** took place only upon prolonged boiling in cyclooctane. The final equilibrium mixture contained 10% of the *trans*- and 90% of the *cis*-isomer as indicated by NMR data. The results show that *cis*-1-trimethylsilyl-1,2-dibromo- and *cis*-1-trimethylsilyl-1,2-diiodoethenes are more stable thermodynamically than their *trans* counterparts.

Table 2

^{13}C and ^1H NMR chemical shifts (δ) for *trans*- (**1**) and *cis*-1-trimethylsilyl-1,2-dihalogenoethenes (**2**) $(C_{\beta'}H_3)_3SiC_\beta X{=}C_\alpha HX$ (X = Cl (**a**), Br (**b**), I (**c**)); all values in ppm relative to TMS

Compound	$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(C_{\beta'})$	$\delta(H_\alpha)$	$\delta(H_{\beta'})$
1a[a]	127.12	136.90	−1.23	7.15	−0.30
2a[a]	123.86	139.37	−2.38	7.35	−0.45
1b[a]	114.12	127.54	−0.35	7.33	0.34
2b[a]	115.93	136.17	−1.81	7.41	0.24
1c[b]	89.68	108.62	0.00	8.08	0.38
2c[b]	102.37	129.00	−0.85	8.20	0.24

[a] Solution in $CDCl_3$. [b] Solution in $(CD_3)_2CO$.

Table 3

$^{13}C,^{13}C$ spin–spin coupling constants (^1J(C=C)) for *trans*- (**1a**–**1c**) and *cis*-1-trimethylsilyl-1,2-dihalogenoethenes (**2a**–**2c**), $(CH_3)_3SiCX{=}CHX$, X = Cl (**a**), Br (**b**), I (**c**), and *trans*- (**3a**–**3d**) and *cis*-1,2-dihalogenoethenes (**4a**–**4d**), XCH=CHX (X = Cl (**a**), Br (**b**), I (**c**), F (**d**))

X	Compound	^1J(C=C) Hz	Ref.	Compound No	^1J(C=C) Hz	Ref.
Cl	**1a**	77.5	[a]	**2a**	67.5	[a]
Br	**1b**	72.4	[a]	**2b**	64.9	[a]
I	**1c**	66.3	[a]	**2c**	62.5	[a]
Cl	**3a**	91.9	[12]	**4a**	84.5	[12]
Br	**3b**	86.4	[a]	**4b**	82.2	[a]
I	**3c**	78.3	[13]	**4c**	78.7	[13]
F	**3d**	121.3	[b]	**4d**	109.8	[b]

[a] This work. [b] INDO/MCI data from ref. 14.

Table 4

^{13}C, ^{1}H and ^{13}C, ^{29}Si spin–spin coupling constants for *trans*- (**1a**–**1c**) and *cis*-1-trimethylsilyl-1,2-dihalogenoethenes (**2a**–**2c**) $(C_{\beta'}H_3)_3SiC_\beta X{=}C_\alpha HX$ [a] (X = Cl (a), Br (b), I (c): all values are in Hz.

Compound	$^{1}J(C_\alpha H_\alpha)$	$^{2}J(C_\beta H_\alpha)$	$^{1}J(C_\beta Si)$	$^{1}J(C_{\beta'}Si)$	$^{3}J(SiH_\alpha)$
1a	198.9	1.2 (0.8)	62.3	[b]	7.1
1b	201.5	1.2 (−0.4)	60.3	55.2	7.8
1c	199.3	1.8 (−1.5)	57.6	54.6	9.6
2a	196.6	21.1 (17.9)	62.3	[b]	2.9
2b	197.1	20.6 (17.3)	59.3	55.0	3.2
2c	191.8	17.6 (12.5)	55.4	54.3	4.1

[a] The figures in parentheses show the values of $^{2}J(CH)$ estimated by the additivity scheme using increments taken from ref. 7. [b] Not determined.

The NMR data obtained for the title compounds are listed in Tables 2–4. Values of ^{13}C chemical shifts (δ) are listed in Table 2, spin–spin coupling constants between carbons of the double bond in Table 3, and ^{1}H-^{13}C and ^{13}C–^{29}Si coupling constants in Table 4.

The assignments of the ^{13}C signals in the ^{13}C NMR spectra (Table 2) were based on magnitudes of $^{1}J(^{13}C^{1}H)$ and $^{1}J(^{13}C^{29}Si)$

For comparison Table 3 also includes data for *trans*-, (**3a**–**3d**), and cis-1,2,-dihalogenoethenes (**4a-4d**), XCH=CHX (X = Cl (**a**), Br (**b**), I (**c**), F (**d**)) either taken from the literature or recorded in our laboratory.

Discussion

Inspection of the IR and NMR data for the compounds studied reveals that three parameters provide a rapid and clear means of distinguishing between the *cis* and *trans* arrangement of halogens about the double bond. These are the intensity of $\nu(C{=}C)$ bands in IR spectrum and the magnitudes of $^{2}J(C_\beta H_\alpha)$ and of $^{3}J(^{29}SiH_\alpha)$ in the NMR spectra. The $\nu(C{=}C)$ bands in the IR spectra of the *trans* isomers are, as predicted by theory, of low to medium intensity, whereas very strong in the spectra of the *cis* isomers.

The three-bond couplings between α-hydrogen and silicon nuclei across the C=C bond are consistently about twice as large for the *trans* than for the *cis* compounds. The $^{3}J(^{29}Si^{1}H_\alpha)$ varies from 7.1 Hz in **1a** to 9.6 Hz in **1c** and from 2.9 Hz in **2a** to 4.1 Hz in **2c**. In both cases, the coupling decreases with increasing electronegativity of the halogen substituent *.

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* A similar relationship for $^{3}J(SiH)$ values across a double bond has recently been reported (M. Grignon-Dubois and M. Lagerre, Organometallics, 7 (1988) 1443) for alkyl-substituted vinylic silanes. However the absolute magnitudes of $^{3}J(SiH)$ reported by these authors are considerably larger and fall in the range 12.6–17.2 Hz for the *trans* and 6.2–13.2 Hz for *cis* compounds.

The difference between $^2J(C_\beta H_\alpha)_{trans}$ and $^2J(C_\beta H_\alpha)_{cis}$ is more pronounced than that for $^3J(^{29}SiH_\alpha)$ values. The value of the $^2J(C_\beta H_\alpha)$ constant for the spectra of the *trans*-isomers is close to zero (1.2–1.8), whereas for the spectra of the *cis* compounds it falls in the range 17.6 Hz (in **2c**) to 21.1 Hz (in **2a**). It is noteworthy that the $^2J(CH)$ couplings analysed in the present work can be estimated by means of the additivity scheme proposed by Weigert and Roberts [6]. The $^2J(CH)$ values calculated from the increments given in ref. 7 agree reasonably well with the experimental values (see Table 4), and this provides an additional proof that the structures of the compounds studied are assigned correctly.

An analysis of the $^1J(C{=}C)$ data, which was the primary objective of our work, showed that: (i) the magnitude of $^1J(C{=}C)$ decreases monotonically with the decreasing electronegativity of the halogen in both *cis*- and *trans*-1-trimethylsilyl-1,2-dihalogenoethenes (compds. **1a**–**1c**, **2a**–**2c**) and in 1,2-dihalogenoethenes (compounds **3d**, **a**–**c** and **4d**, **a**–**c**), (ii) the value of $^1J(C{=}C)_{trans}$ is generally larger than that of $^1J(C{=}C)_{cis}$, but the difference diminishes in both groups studied with decreasing electronegativity of the halogen: thus, e.g., Δ^1J(**4d**–**3d**) > Δ^1J(**4a**–**3a**) > Δ^1J(**4b**–**3b**) > Δ^1J(**4c**–**3c**) ($E_F > E_{Cl} > E_{Br} > E_I$), and the difference is negligible for the 1,2-diiodoethenes, **3c** and **4c**, $^1J(C{=}C)$ in *cis* isomer being slightly larger (by 0.4 Hz) than in the *trans* form. The differences in $^1J(C{=}C)$ values tend to reflect the differences in energy between *cis* and *trans* isomers. Available data [8] indicate that *cis*-1,2-difluoroethene is more stable than the *trans*-isomer by 3.9 kJ/mol. The difference is smaller for 1,2-dichloro- and 1,2-dibromo-ethenes (2.7 and 1.3 kJ/mol, respectively) and is close to zero for 1,2-diiodoethenes, *cis*-1,2-diiodoethene being less stable than its *trans*-isomer [9].

We cannot offer a theoretical justification for the observed relationship between $\Delta^1J(C{=}C)$ and ΔE. It is, however, well known that spin–spin coupling constants $^1J(CC)$, including those across C=C double bonds, depend upon the relevant contributions of the *s*-electrons to the corresponding bonding orbitals [10]. The observed decreases in $\Delta^1J(C{=}C)$ (*trans*–*cis*) and in ΔE (*trans*–*cis*) can therefore be tentatively associated with the *s*-electrons densities of the bonding orbitals of the *cis* and *trans* isomers.

We now consider the $^1J(C{=}C)$ data from the point of view of multiplicativity and/or additivity effects. As mentioned in the Introduction, the value of $^1J(C_AC_B)$ in any molecule can be calculated as described by Egli and Philipsborn [2], as the product of two empirical factors I_{C_A} and I_{C_B} (eq. 3). The factors I can be calculated as the square roots of the values of $^1J(CC)$ in the corresponding symmetrical molecules (key factors) or from values for unsymmetrical molecules of any kind by dividing the experimental CC coupling constant by the corresponding key factors.

We recently suggested in considering spin–spin coupling constants $^1J(C{=}C)$ for fluoro-substituted ethylenes [11] that in a further step the factors I could be separated by use of equation 5 in which the increments i_X and i_Y are the

$$I_{(XYC=)} = i_X + i_Y \tag{5}$$

contributions associated with the substituents X and Y, respectively. Knowledge of the I_X and i_X contributions characteristic of a given substituent, and relationships between them and the configuration of the compounds may be useful in estimating unknown $^1J(C{=}C)$ values. We have calculated the factors $I_{(HXC=)}$ (*trans* and *cis*) and the corresponding increments i_X for X = Cl, Br, I from the J data for

Table 5

The values of the I factors and i increments calculated from the data for 1,2-dihalogenoethenes (**3a**–**3c** and **4a**–**4c**) and 1-trimethylsilyl-1,2-dihalogenoethenes (**1a**–**1c** and **2a**–**2c**); all values are in $\mathrm{Hz}^{1/2}$.

moiety	I [a]	moiety	i [b]	moiety	i [c]
trans					
HClC=	9.60	ClC=	5.47	$(CH_3)_3SiC=$	2.61
HBrC=	9.30	BrC=	5.18	$(CH_3)_3SiC=$	2.61
HIC=	8.85	IC=	4.73	$(CH_3)_3SiC=$	2.76
cis					
HClC=	9.19	ClC=	5.08	$(CH_3)_3SiC=$	2.27
HBrC=	9.07	BrC=	4.95	$(CH_3)_3SiC=$	2.21
HIC=	8.87	IC=	4.76	$(CH_3)_3SiC=$	2.29

[a] Calculated from the data for compounds **3** and **4** (Table 3). [b] Calculated by subtracting $i_{CH=}$ 4.11 $\mathrm{Hz}^{1/2}$ (see ref. 11) from the corresponding I value. [c] Calculated from the J data for compounds **1-2** and the corresponding $I_{HalC=}$ and $i_{HalC=}$ values.

compounds **3a**–**3c** and **4a**–**4c**. The $i_{(CH_3)_3Si}$ increments were derived by use of the latter values and the data for compounds **1a**–**1c** and **2a**–**2c**. An inspection of the results (Table 5) reveals that the magnitudes of the factors I and of the increments i depend on the configuration of the compound in question. For example, $i_{(CH_3)_3Si}$ is constant for a given series (*cis* and *trans*) of the compounds, but $i_{(CH_3)_3Si}$ (*trans*) is considerably greater than $i_{(CH_3)_3Si}$ (*cis*). The influence of the configuration on the value of I and i introduces a serious limitation on the general applicability of multiplicativity/additivity scheme for estimation of unknown $^1J(C{=}C)$ values. On the other hand, analysis of relationships between increments for a large and representative set of data may perhaps provide a valuable source of information about the distribution of electrons in a given molecule.

We finally comment on the NMR data for the compounds examined that we have not discussed above. One-bond ^{13}C, ^{29}Si spin–spin coupling constants clearly depend upon the electronegativity of halogen substituents (Table 4). The largest $^1J(C_\beta Si)$ were found for 1-trimethylsilyl-1,2-dichloroethenes (**1a** and **2a**) (62.3 Hz for both isomers) and the smallest for 1-trimethylsilyl-1,2-diiodoethenes (**1c** and **2c**) 57.6 and 55.4 Hz, respectively.

There is an interesting, though perhaps fortuitous relationship between the spin–spin coupling constants $^1J(CH)$ and the sum of $^1J(C{=}C)$ and $^1J(CH)$. The changes in $^1J(CH)$ (see Table 4) for 1-trimethylsilyl-1,2-dihalogenoethenes are rather irregular and cannot be interpreted in terms of the influence of electronegativity of substituent. However, the sum of $^1J(CH)$ and $^1J(C{=}C)$ decreases monotonically with the E_X value for the substituent for both the *cis* and the *trans* series, the sum for the *trans* isomer being consistently greater, by 11–12 Hz, than that for the *cis* isomer.

Inspection of the ^{13}C chemical shift data listed in Table 2 reveals significant differences between the chemical shifts of the corresponding carbon atoms of the geometrical isomer concerned. Particularly large differences in ^{13}C shifts for both the α and β carbons were found between compounds **1c** and **2c** (diiodo *cis* and *trans* derivatives). They decrease on passing to the dibromo *cis* and *trans* compounds **1b** and **2b**, and then further to *trans*- and *cis*-1-trimethylsilyl-1,2-dichloroethenes (**1a** and **2a**). For the α-carbon in the latter pair of compounds even the sign

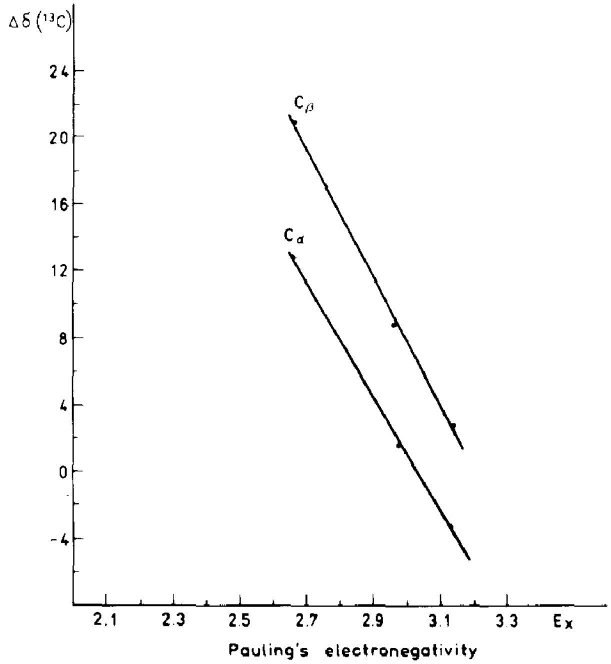

Fig. 1. Plots of the differential shieldings of the α and β carbons, $\Delta = \delta$ *cis* $- \delta$ *trans*, against the Pauling electronegativity of the halogen substituent for $(CH_3)_3SiCX{=}CHX$ compounds (X = Cl, Br, I).

of the difference changes. These observations are consistent with that made by Savitski and co-workers who studied the influence of *cis–trans* isomerism on the ^{13}C chemical shifts for halogen-substituted ethenes and alkenes [15,16]. Several explanations, including charge separation and reduced bond order in the C=C π-bond of *cis* isomers, were suggested by these authors to account for the differences in the ^{13}C shifts of the isomeric pairs [16]. Such factors are also likely to play some role in the case of the compounds examined in the present work, but it is noteworthy that the magnitudes of the *cis-trans* $\Delta\ \delta$ (^{13}C) values for both of the ethylenic carbons decrease with increasing electronegativity of the halogen. Moreover, the relationship seems to be quite linear (see Fig. 1), but because of the limited number of data, the corresponding equations cannot be derived.

We conclude that the results obtained in the present work show that the substituuent electronegativity is a major factor governing the electron distribution in *trans*- and *cis*-1-trialkylsilyl-1,2-dihalogenoethenes.

Experimental

Synthesis and isomerization of the compounds. General remarks

During the syntheses of **1a** and **1b** (dichloro-*trans* and dibromo-*trans* derivatives) all operations were carried out with exclusion of light. When the reaction was over traces of halogen were carefully removed; this prevented isomerization of the product to the *cis* form, and subsequent operations could be carried out in daylight. In contrast the *trans* diiodo compound **1c** could be obtained only when a mixture of trimethylsilylethyne and iodine was irradiated with strong light. *Cis* isomers were prepared either by an addition of halogen to trimethylsilylethyne in the presence of light (**2b**) or by isomerization of the corresponding *trans* species (compds. **2a**–**2c**). Samples of **1a**, **1b**, **2a** and **2b** were purified, if necessary, by means of GLC with a Varian Model 920 gas chromatograph fitted with a column of 10% SE-30 on Chromosorb W. Samples of **1c** and **2c** were purified by TLC on silica gel plates with heptane as eluent. In the GLC (compds. **1a**, **2a** and **1b**, **2b**) the retention time for a *trans* isomer was smaller than that for the related *cis* isomer. In thin-layer chromatography of the compounds **1c** and **2c** the R_F value for the *trans* isomer was larger than that for the *cis* isomer. The ratio of *cis* to *trans* forms in final products was established chromatographically and checked by ^{1}H NMR spectroscopy.

Synthesis of trans isomers

trans-1-Trimethylsilyl-1,2-dichloroethene (1a). A solution of 0.3 g (4.2 m*M*) of chlorine in 3 cm^3 of CCl_4 was slowly added with vigorous stirring to a solution of 0.5 g (5 m*M*) of trimethylsilylethyne in 20 cm^3 of CCl_4 containing 30 mg of reduced Fe. The temperature was kept at 0 °C. The mixture was allowed to warm up to room temperature then left overnight. Inorganic salts were then removed by decantation and the organic layer washed twice with cold saturated aqueous solution of sodium sulphite, twice with cooled diluted HCl, then three times with ice water, and finally dried over $MgSO_4$. The solvent was evaporated off under vacuum and the residual oil was purified by chromatography as described above, 0.29 g (35% of theor.). Analysis: Found: C, 35.46; H, 5.91; Cl, 42.08. Calcd.: C, 35.46; H, 5.99; Cl, 42.20%.

trans-1-Trimethylsilyl-1,2-dibromoethene (**1b**) was obtained as described for **1a** but starting from 0.5 g (5 m*M*) of trimethylsilylethyne in 20 cm^3 of CCl_4 and 0.6 g (3.8 m*M*) of bromine in 5 cm^3 of CCl_4. The yield of crude oil was 0.6g (47% of theor.).

trans-1-Trimethylsilyl-1,2-diiodoethene (**1c**) was made essentially as described in ref. 5 starting from 0.5 g of trimethylsilylethyne (5 m*M*) and 0.63 g (5 m*M*) of iodine. The mixture was irradiated for 7 h with a UV lamp (λ 254 nm). The obtained crude oil (0.85 g, 48% of theor.) was worked up as described for **1a** and purified by TLC.

cis Isomers

Isomerization of trans isomers under influence of light

cis-1-Trimethylsilyl-1,2-dichloroethene (2a). A solution of 20 mg of **1a** in 1 cm^3 of CCl_4 was placed in a quartz glass vessel, a minute amount of bromine was added, and the solution was irradiated with a UV lamp for 30 min. The final product consisted of an 8/92 *trans*/*cis* mixture. No by-products were observed. Direct addition of chlorine to trimethylsilylethyne under UV irradiation gave a mixture of several products that were rather difficult to separate, and were not identified. Only isomerization of the *trans* isomer was used for synthesis of **2a**.

cis-1-Trimethylsilyl-1,2-dibromoethene (2b). (i) A solution of 20 mg of **1b** was treated as described above for **1a**. The *cis* to *trans* ratio in the final mixture was 95 to 5. (ii) To a solution of 0.5 g (5.0 m*M*) of trimethylsilylethyne in 20 cm^3 of CCl_4, 0.6 g (3.8 m*M*) of bromine was added in several portions. The solution was irradiated with a UV lamp and the course of reaction monitored by GLC. The ^{1}H NMR peak from the *trans* isomer which was very strong at first disappeared rapidly, and when the addition of Br_2 was complete the *cis* to *trans* ratio was again 95/5. No by-products were observed. Yield 0.9 g (92% based on Br_2).

Isomerization of trans isomers under influence of heat

*cis-1-Trimethylsilyl-1,2-dibromoethene (**2b**).* A solution of 20 mg of *trans*-1-trimethylsilyl-1,2-dibromoethene (**1b**) in 1 cm^3 of cyclooctane was treated with a very small amount of bromine (less than 1 mg). The solution was refluxed (154 °C) for 16 h with careful protection from the light. Samples taken to check the ratio of isomers were also protected from the light. After 12 h the ratio of *cis* to *trans* isomers was 95 to 5, and did not change during a further 4 h. No by-products were observed.

*cis 1-Trimethylsilyl-1,2-diiodoethene (**2c**).* A solution of 1.5 g of **1c** in 10 cm^3 of cyclooctane was boiled (in the dark) under reflux (154 °C) for 24 h. After 20 h the ratio of *cis* to *trans* isomers was 90 to 10, and did not change during a further 4 h. Some decomposition of the compounds, involving less of iodine, was observed. Yield 1.2 g (80% of theor.).

*Synthesis of trans (**3b**) and cis-1,2-dibromoethenes (**4b**)*

*trans- and cis-1,2-dibromoethenes (**3b** and **4b**).* These were synthesized by reduction of 1,1′,2,2′-tetrabromoethane with zinc in ethanol, as described in ref. 17. This gave a mixture of *cis* and *trans* isomers of 1,2-dibromoethene in a 3/2 ratio as estimated from the relative heights of the relevant peaks in NMR. No attempt was made to separate the *cis–trans* mixture, and it was used for all the NMR measurements performed on compounds **3b** and **4b**. The assignment of peaks in NMR to *cis* and *trans* isomers was based on that in ref. 15.

Measurements

The ^{1}H and ^{13}C NMR spectra were recorded for samples in 5 mm tubes with a Bruker AM 500 spectrometer or sometimes a Bruker WP-100 SY instrument. All the proton-decoupled NMR spectra were recorded twice, without and with a small amount of TMS present, and this allowed accurate determination of the positions of the signals from the carbon atoms and protons of the $(CH_3)_3Si$ group. Chloroform-d_1 and acetone-d_6 were used as solvents. Typical conditions used to record a ^{1}H spectrum were: acquisition time 5–8.35 s, digital resolution 0.07–0.12 Hz/point, number of transients 30–80, and standard ^{13}C spectrum: acquisition time 1.31–4.85 s, digital resolution 0.30–0.76 Hz/point, number of transients 35–280.

The ^1J(CH) and ^2J(CH) couplings were determined from ^{13}C-proton H_α coupled spectra, with the protons of $(CH_3)_3Si$ group decoupled. This was particularly important for observation of the small $^2J(C_\beta H_\alpha)$ couplings for compounds **1a**–**1c**, which were obscured by larger couplings of C_β with the nine protons of the silyl group in fully ^{1}H-coupled spectra. Typical conditions were as follows: acquisition time 7.25–8.43 s, digital resolution 0.14–0.80 Hz/point, number of transients 25–150.

The ^1J(SiC) and ^3J(SiH) coupling constants were derived from the ^{29}Si satelite spectra in the corresponding ^{13}C and ^{1}H spectra.

All C,C spin–spin coupling constants were determined at natural ^{13}C abundance by means of the INADEQUATE technique. In the case of the compounds **1a**–**1c** and **2a**–**2c** the recorded ^{13}C-proton decoupled satellite spectra corresponded to an AB type spin systems, and the relevant coupling constants were determined directly from the spectrum. The values of ^1J(C=C) for the symmetrically substituted dibromoethenes **3b** and **4b** were determined from satellite ^{13}C-proton coupled spectra which appeared as AA′XX′ spin system (see ref. 12). All INADEQUATE spectra were recorded by means of the standard Bruker microprogram; devised by Freeman typical conditions were: acquisition time 2.4–6.2 s, digital resolution 0.160–0.250 Hz/point, number of cycles 224–600.

Measurements of dipole moments

Dielectric permitivities, ϵ, were determined with CCl_4 solutions at (25 ± 0.1)°C by use of a Dipole meter DM-01 equipped with cell type DF L 1/s (Wissenschaftlisch-Technische Werkstätten, Weillheim). The accuracy of the measured capacitance was 0.05%. Refractive indices, n, were determined with a conventional Abbe refractometer with an accuracy of 5×10^{-5}. Densities of solutions, d, were determined pycnometrically with an accuracy of 3×10^{-4} g cm^{-1}. Molar polarization was calculated by the Hedestrand dilute-solution procedure [18]. IR spectra were recorded on a Beckman IR 4240 spectrometer.

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