

THE STEREOCHEMISTRY OF THE ADDITION OF DICHLOROSILANE TO ACETYLENES

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Summary

The stereochemistry of the addition of dichlorosilane to five substituted acetylenes was studied in the presence of three catalyst systems: chloroplatinic acid, platinum on carbon, and benzoyl peroxide. Platinum-catalyzed additions proceeded in a stereospecific *cis* fashion yielding *trans* adducts. Products of additions to terminal acetylenes also included internal adducts and novel bis-(*trans*-dialkenyl)dichlorosilanes. A large excess of dichlorosilane was necessary to minimize formation of the bis adducts since the mono adducts seemed to add to the acetylenes more rapidly than dichlorosilane itself. Both the yields and ratio of the internal (addition to C-2) to *trans* terminal adducts were remarkably similar for both platinum catalyst systems. Peroxide-catalyzed additions gave predominantly *cis* adducts except for 3,3-dimethyl-1-butyne which gave largely *trans*. It was demonstrated that the *cis* adduct in this case was in part isomerized to *trans* in the presence of dichlorosilane and benzoyl peroxide and that a portion was diverted to high-boiling materials.

Introduction

Few examples of addition reactions of dichlorosilane are cited in the chemical literature and of these none are with acetylenes. We have previously described the stereochemistry of trichlorosilane additions to acetylenes [1–3]. The recent commercial availability of dichlorosilane*, coupled with our recent findings with regard to its unusual additions to olefins [4], prompted an investigation into its platinum- and peroxide-catalyzed additions to a series of simple acetylenes. This paper describes the stereochemical course of these reactions and introduces many new compounds among which are the novel bis(*trans*-dialkenyl)dichlorosilanes.

* Obtained from Union Carbide Corporation, Sistersville, West Virginia.

Results and discussion

Dichlorosilane adds spontaneously at room temperature to simple terminal acetylenes when catalyzed by chloroplatinic acid to give a *trans* terminal adduct. In addition, two other products generally constituted a considerable portion of the isolated adducts.

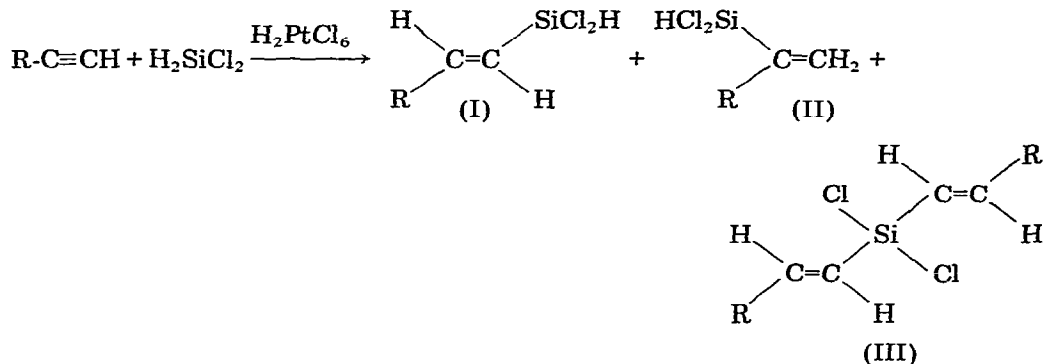


Table 1 gives results of addition performed with 200 mmole of dichlorosilane and 100 mmole acetylene. Structural assignments on the *trans* geometry of the terminal monoadduct (I) and the dialkenyldichlorosilane (III) were made by examination of their IR and NMR spectra. Peaks considered diagnostic of a *trans* configuration [5,6] were observed at 10.17μ in the IR spectra. Also, typically large *trans* coupling constants [7] of 18.5 Hz were noted in the NMR spectra. Finally, the *trans* geometry was confirmed by methylation of dichlorosilyl adducts and authentic samples of *trans* trichlorosilyl adducts [1,2]. The trimethylsilyl derivatives derived from both were identical.

The ratio of terminal to internal adduct in the platinum-catalyzed addition was approximately 80/20 in the case of the terminal acetylenes. One exception was tert-butylacetylene which gave only *trans* terminal monoadduct. The bulky

TABLE I
PLATINUM-CATALYZED ADDITIONS OF DICHLOROSILANE TO ACETYLENES

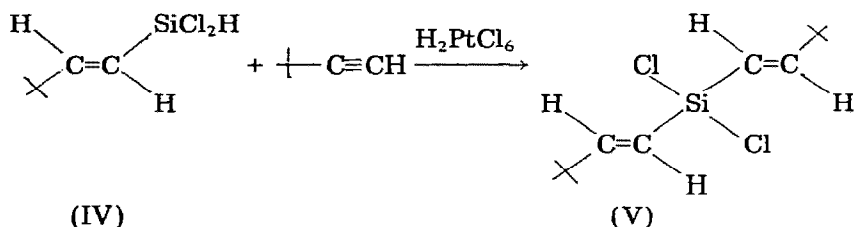
Acetylene	Catalyst [time (h), temp (C°)]	Yield (%)		
		(I) ^a	(II) ^a	(III) ^a
1-Pentyne	H ₂ PtCl ₆ (3, RT)	56	15	19
	Pt/C (3, 60)	44	13	30
	Pt/C (3, 100)	48	14	17
1-Hexyne	H ₂ PtCl ₆ (3, RT)	52	12	16
	Pt/C (3, 65)	48	10	7
1-Octyne	H ₂ PtCl ₆ (3, RT)	47	13	15
	Pt/C (3, 70)	52	12	15
tert-Butylacetylene	H ₂ PtCl ₆ (3, 60)			12
	Pt/C (3, 60)			
	Pt/C (3, 120)	34		6
3-Hexyne	H ₂ PtCl ₆ (24, 120)		88 ^b	

^a All compounds gave acceptable elemental analyses, IR and NMR spectra. ^b *cis*-3-(Dichlorosilyl)-3-hexene.

tert-butyl group sterically inhibited attachment of Si to C-2 and also lowered the reactivity of the acetylene towards addition. Only tert-butylacetylene and the disubstituted acetylene, 3-hexyne, required any heating to effect addition with chloroplatinic acid catalyst.

The presence of dialkenyldichlorosilanes (III) was surprising in light of the 2/1 excess of dichlorosilane employed. A 4/1 excess of dichlorosilane with 1-hexyne still resulted in a 6% yield of bis(*trans*-1-hexenyl)dichlorosilane. When a 2.5/1 excess of 1-hexyne to dichlorosilane was employed, none of the mono-adduct was found.

To demonstrate the reactivity of a mono adduct toward further addition, *trans*-3,3-dimethyl-1-(dichlorosilyl)-1-butene (IV), tert-butylacetylene and chloroplatinic acid were combined at room temperature. A rapid exothermic addition ensued without additional heating, yielding 96% of bis(*trans*-3,3-dimethyl-1-butenyl)dichlorosilane (V). Dichlorosilane does not add to tert-butylacetylene without external heating.



Results of additions catalyzed by 30% platinum on carbon are also given in Table 1, which show similarity both in internal/terminal adduct ratios and in yields of both platinum catalysts.

The results of peroxide-catalyzed additions are given in Table 2. All the monoadducts were mixtures of *cis* and *trans* isomers. These were methylated when they proved too difficult to separate by VPC, then subjected to capillary

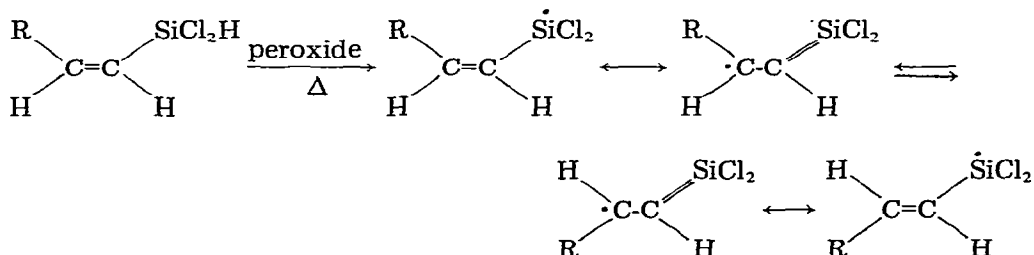
TABLE 2
BENZOYL PEROXIDE-CATALYZED ADDITIONS OF DICHLOROSILANE TO ACETYLENES

Acetylene	Temp. (°C)	Time (h)	Reaction vessel	Isomer distribution ^a		Yield ^b (%)
				<i>cis</i> (%)	<i>trans</i> (%)	
1-Pentyne	120	19	Bomb	52	48	33 ^c (75)
	120	20	Carius tube	61	39	32 ^c (70)
1-Hexyne	130	19	Bomb	54	46	27 ^c (82)
	110	20	Carius tube	62	38	29 ^c (70)
tert-Butylacetylene	110	16	Bomb	20	80 ^d	26
3-Hexyne	130	24	Bomb	34	66 ^e	41 (72)
	125	20	Carius tube	33	67 ^f	58

^a Assigned on the basis of peak areas exhibited by the methylated adducts on a VPC trace taken on a Perkin Elmer 126 capillary gas chromatograph with an apiezon L and polyphenyl ether dual column.

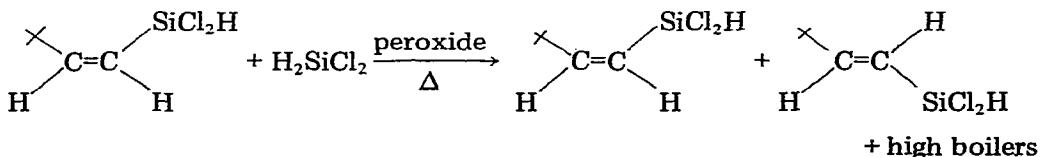
^b The value in parenthesis is the yield (based on dichlorosilyl adduct) of the methylation with an ethereal solution of methylolithium. ^c Does not include a 1–2% yield of internal adduct noted in these reactions. ^d *Cis* and *trans* isomers were easily separated without methylation on an SE-30 column. ^e Here the *trans* isomer arises from *trans* addition. ^f Two distinct silicon-hydrogen peaks in the NMR spectrum of *cis* and *trans* adducts with a ratio of 2/1 were used to assign an approximate isomer distribution.

VPC analysis and identified by coinjection with methylated authentic samples of *cis* and *trans* trichlorosilyl adducts [1,2]. Some difference in the *cis/trans* monoadduct ratio of 1-pentyne and 1-hexyne was noted when the reactions were run in Carius tubes rather than in stainless steel bombs. Both acetylenes gave $\approx 50/50$ *cis/trans* isomer ratios in a bomb and 60/40 in glass. Blank runs in the stainless steel bomb revealed some catalysis by the bomb itself. Very likely, metals in the bomb itself catalyze the reaction much as does platinum, thereby leading to an increased yield of the *trans* isomer. However, the 3/2 *cis/trans* monoadduct ratio found in the Carius tubes still differed from the 3/1 ratio obtained for the corresponding trichlorosilane additions [2]. There are several possible explanations for this difference in stereospecificity of addition between di- and trichlorosilane. Possibly the addition of the dichlorosilyl radical is intrinsically less stereospecific than the trichlorosilyl radical, or perhaps the *cis* dichlorosilyl adduct undergoes a more facile isomerization to *trans*. The latter could conceivably proceed via a dichlorosilyl adduct radical, a pathway not available to the trichlorosilyl adducts. A third possibility is that the dichlorosilyl



adduct radical depicted in the equation above, undergoes further addition leading to higher boiling products which are indeed observed. It is quite conceivable that such subsequent additions might proceed more rapidly with the *cis* monoadducts than the *trans*, and thus give a deceptive picture as to the true stereoselectivity of the initial addition. Some evidence was obtained which lends credence to the two latter explanations.

The hindered *tert*-butylacetylene unexpectedly gave an 80/20 *trans/cis* adduct ratio in peroxide-catalyzed addition. The ease of separation of the two isomeric adducts by VPC invited the isolation and use of the pure *cis* isomer to determine its stability in the presence of dichlorosilane and benzoyl peroxide. After heating *cis*-3,3-dimethyl-1-(dichlorosilyl)-1-butene at 120° for 20 h, only 54% of low boiling material was recovered as a mixture of *cis* and *trans* adducts (15/85). Clearly *both* isomerization of *cis* to *trans* isomer was occurring



in this case as well as competing side reactions leading to higher boiling products and destruction of the initial *cis* adduct. It seems likely, therefore, that the peroxide-catalyzed additions of dichlorosilane are much more stereospecific than the 3/2 *cis/trans* ratio of products would indicate.

In order to establish that benzoyl peroxide was actually participating in the reactions carried out in Carius tubes, and that the products obtained were not simply the result of a thermal process, blank runs were made with 1-hexyne and 3-hexyne in the presence of dichlorosilane alone. Only a 6% yield was realized with 1-hexyne and a 2% yield with 3-hexyne.

A major difference in peroxide- vs. platinum-catalyzed additions was the internal/terminal adduct ratio. The internal isomer from peroxide-catalyzed additions may well have been produced initially in the same proportion as in platinum-catalyzed additions, but was rapidly depleted by further reaction to higher boiling adducts. When monoadducts obtained from platinum-catalyzed addition of dichlorosilane to 1-hexyne (75/25 terminal/internal) were combined with dichlorosilane and benzoyl peroxide at 110° for 20 h, the ratio reverted to 96/4 (55% recovery), a value typical of peroxide-catalyzed additions. Several unidentified higher boiling products accounted for the loss of monoadduct. If one views the adducts as a terminal olefin and an internal olefin then a rational explanation for this behavior exists since terminal olefins are more reactive towards radical additions than internal olefins [8–10].

Experimental

All distillations were performed with microwave apparatus and the boiling points are uncorrected. Separations of dichlorosilyl adducts were done on a preparative scale VPC with a 9' × 3/8" SE-30 column. Methylated *cis* and *trans* adducts were separated on a Perkin–Elmer Model 226 capillary VPC using an apiezon L and polyphenyl ether dual column. The *cis/trans* ratios were calculated by triangulation of peaks. The IR spectra were recorded on a Perkin–Elmer Model 137 spectrometer and the NMR spectra on a Varian Model A-60 spectrometer. Elemental analyses were performed in the microanalytical laboratory of Purdue University by Dr. C.S. Yeh.

Chloroplatinic acid-catalyzed addition of dichlorosilane

The same general procedure was used in all runs as described below for the addition to 1-pentyne.

A 150 cc stainless steel bomb was charged with 6.8 g (0.10 mole) 1-pentyne, 50 μ l chloroplatinic acid solution*, and 20.2 g (0.20 mole) dichlorosilane. Immediately after an exothermic reaction ensued, the contents were cooled to avoid decomposition. After 3 h at room temperature, distillation in vacuo afforded two fractions: (1) 11.9 g (b.p. 68–73° at 50 mm); (2) 3.3 g (b.p. 77–85° at 1.9 mm). The adducts and yields are given in the order of their elution from an SE-30 column. (1) *trans*-1-(Dichlorosilyl)-1-pentene (56%). (Found: C, 35.63; H, 5.88; Cl, 41.80; Si, 16.49, C₅H₁₀Cl₂Si calcd.: C, 35.51; H, 5.96; Cl, 41.92; Si, 16.61%.) (2) 2-(Dichlorosilyl)-1-pentene (15%). (Found: C, 35.32; H, 5.80; Cl, 41.63; Si, 16.40, C₅H₁₀Cl₂Si calcd.: C, 35.51; H, 5.96; Cl, 41.92; Si, 16.61%.) (3) Bis-(*trans*-1-pentenyl)dichlorosilane (19%). (Found: C, 50.36; H, 7.86; Cl, 30.09; Si, 11.60, C₁₀H₁₈Cl₂Si calcd.: C, 50.63; H, 7.65; Cl, 29.89; Si, 11.84%.)

* Prepared by adding 2 ml of isopropyl alcohol to 0.10 g of H₂PtCl₆ · 6H₂O (Englehard Industries, Inc.).

Platinum-on-carbon-catalyzed additions of dichlorosilane

The above procedure was duplicated with 0.03 g of 30% platinum on carbon [11] as catalyst. After the bomb was charged, its contents were heated at specified temperatures for the indicated periods.

Benzoyl peroxide-catalyzed dichlorosilane additions

The same procedure as above was employed with 1.6 g of benzoyl peroxide as catalyst. The addition to 1-pentyne described below is typical.

A mixture of 6.8 g (0.10 mole) 1-pentyne, 1.6 g benzoyl peroxide, and 20 g (0.20 mole) dichlorosilane was heated at 120° for 19 h. Distillation afforded two fractions: (1) 6.0 g (b.p. 70 - 82° at 68 mm); (2) 1.7 g (b.p. 95 - 125° at 2.0 mm). The lower-boiling fraction was a mixture of *cis*- and *trans*-1-(dichlorosilyl)-1-pentene (33% yield). (Found: C, 35.69; H, 5.90; Cl, 41.70; Si, 16.89. C₅H₁₀Cl₂Si calcd.: C, 35.51; H, 5.96; Cl, 41.92; Si, 16.61%.) The second contained many components, none of which was identified.

Treatment of the *cis/trans* mixture with methylmagnesium iodide afforded a 75% yield of *cis*- and *trans*-1-(trimethylsilyl)-1-pentene (52/48). Coinjection with an authentic sample [2] on a capillary VPC as well as comparison of IR spectra confirmed their identity.

Isomerization of cis-3,3-dimethyl-1-(dichlorosilyl)-1-butene

A thick-walled glass tube was charged with 0.0580 g (0.317 mmole) *cis*-3,3-dimethyl-1-(dichlorosilyl)-1-butene, 0.1 g benzoyl peroxide, 45 μ l (0.63 mmole) dichlorosilane and 79 μ l (0.41 mmole) decane as a standard. After heating at 120° for 20 h, the sealed tube was opened and its contents were analyzed by VPC. A 54% recovery of monoadduct was realized as a mixture of *cis* and *trans*-3,3-dimethyl-1-(dichlorosilyl)-1-butene (15/85). Unidentified high boilers were also noted.

Carius tube blanks

1-Hexyne (100 mmole) and dichlorosilane (200 mmole) were heated in a sealed Carius tube at 110° for 20 h. The usual work-up gave 7% of monoadducts. When 3-hexyne (100 mmole) and dichlorosilane (200 mmole) were heated at 125° for 20 h in a similar fashion, a 2% yield of monoadducts was realized. In both runs the *trans*-terminal/internal isomer ratio and NMR spectra matched that of peroxide catalyzed additions.

Stainless steel bomb blanks

A previously unused bomb was charged as described above with 8.2 g (11.5 ml, 0.10 mole) 1-hexyne and 20.2 g (14.2 ml, 0.20 mole) dichlorosilane. It was heated in an oil bath at 95° for 20 h and the contents worked up as before. These was obtained 2.7 g (b.p. 85 - 88° at 44 mm). Analysis by VPC showed 93% of the distillate was monoadduct in an 83/17 *trans*-terminal/internal ratio (14% yield). Spectral analysis confirmed the adducts were the same as those isolated in platinum-catalyzed additions.

The above reaction was repeated in a bomb which had previously been used for platinum-catalyzed additions but cleaned with potassium hydroxide solution followed by an acid wash. A 32% yield of monoadducts was obtained

(81/19 *trans* terminal/internal ratio) and a 3% yield of bis(*trans*-1-hexenyl)-dichlorosilane after only 3 h heating at 65%.

Acknowledgement

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