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ADDITION OF CHLORODISILANES TO ACETYLENE CATALYZED BY TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0). A FACILE ROUTE TO (*Z*)-1,2-BIS(CHLOROSILYL)ETHENES

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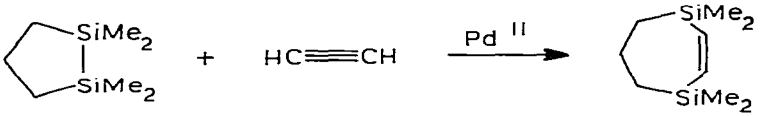
Summary

In the presence of a catalytic amount of tetrakis(triphenylphosphine)-palladium(0), chlorodisilanes of type $Me_nSi_2Cl_{6-n}$ (n = 2—5) add to acetylene to afford 1,2-bis(chlorosilyl)ethenes in reasonable yields.

Introduction

It has been shown recently that disilanes of type $Me_nSi_2X_{6-n}$ (n = 2—6; X = H, F, OMe) or 1,2-disilacycloalkanes undergo addition reactions to the triple bonds of substituted acetylenes (e.g., dimethyl acetylenedicarboxylate, 3-hexyne, phenylacetylene, diphenylacetylene, etc.), in the presence of palladium(0) or palladium(II) complexes [1—4]. However, the addition of disilanes to acetylene has not yet been reported except for one case. Thus, Sakurai and his coworkers have disclosed that acetylene reacted with a strained disilacycloalkane, 1,1,2,2-tetramethyl-1,2-disilacyclopentane, in the presence of $PdCl_2(PPh_3)_2$ to afford 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-ene in 53% yield [2].



(1)

The present paper deals with the addition of strain-free acyclic disilanes of type $Me_nSi_2Cl_{6-n}$ (n = 2—5) to acetylene, leading to 1,2-bis(chlorosilyl)ethenes, and describes several features of this addition reaction.

Results and discussion

It was found that methylchlorodisilanes, such as 1,1,2,2-tetrachloro-1,2-dimethyldisilane, 1,1,2-trichloro-1,2,2-trimethyldisilane, 1,2-dichloro-1,1,2,2-

TABLE 1

ADDITION OF CHLORODISILANES TO ACETYLENE IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0) [a]

Disilane	Conditions (°C/h)	1,2-Bis(chlorosilyl)-ethenes obtained	Yield (%) [b]	Stereochemistry [c] (Z)/(E)
$Cl_2MeSiSiMeCl_2$	80/3	$Cl_2MeSiCH{=}CHSiMeCl_2$ (I)	96	79/21
$Cl_2MeSiSiMe_2Cl$	80/10	$Cl_2MeSiCH{=}CHSiMe_2Cl$ (II)	34	80/20
$ClMe_2SiSiMe_2Cl$	130/7	$ClMe_2SiCH{=}CHSiMe_2Cl$ (III)	78	89/11
$ClMe_2SiSiMe_3$ [d]	120/10	$ClMe_2SiCH{=}CHSiMe_3$ (IV)	55 [e]	93/7

[a] Reactions were conducted by bubbling acetylene gas through a toluene or xylene solution containing a disilane and the palladium(0) complex (1 mol %) unless otherwise stated. [b] Determined by GLC (based on the disilane charged). [c] Determined by GLC and NMR analyses. [d] The catalyst concentration was 2 mol %. [e] Conversion of the disilane charged was 90%.

tetramethyldisilane and chloropentamethyldisilane, react readily with acetylene in the presence of tetrakis(triphenylphosphine)palladium(0) to give the corresponding 1/1 adducts.

$$Cl_mMe_{3-m}SiSiMe_{3-n}Cl_n + HC{\equiv}CH \xrightarrow{Pd(PPh_3)_4} Cl_mMe_{3-m}SiCH{=}CHSiMe_{3-n}Cl_n$$

$$(m = 1, 2; n = 0, 1, 2) \qquad (2)$$

The addition could be conducted simply at the temperature range of 80—130°C by bubbling acetylene gas through a toluene or xylene solution containing the chlorodisilane in the presence of a catalytic amount (1 or 2 mol%, based on the disilane charged) of the palladium(0) complex. The results are listed in Table 1. Structural assignments for the 1/1 adducts were made, after isolation by GLC separation or distillation, based on their IR and NMR parameters and comparison with reported values. The spectral data of the 1,2-bis(chlorosilyl)-ethenes and the results of elemental analyses are given in Table 2.

Inspection of Table 1 shows that the addition of tetrachlorodimethyldisilane and dichlorotetramethyldisilane proceeded smoothly to give the corresponding 1,2-bis(chlorosilyl)ethenes in good yields. A comparison of the reaction conditions for both additions indicates that replacement of a methyl group by a chlorine atom on silicon increases the reactivity of the disilanes. This trend was further confirmed by a competition experiment in which these two disilanes were allowed to react with acetylene at 100°C. The dichlorotetramethyldisilane did not react until most of the tetrachlorodimethyldisilane was consumed. The observed trend also parallels the reported reactivity order of methylchlorodisilanes toward the palladium(0)-catalyzed double silylation of 1,3-butadiene [5].

In contrast to the symmetrical disilanes, the addition of 1,1,2-trichloro-1,2,2-trimethyldisilane to acetylene gave the 1/1 adduct in only 34% yield. The observed low yield is likely to be due to the concurrent occurrence of disproportionation involving Si—Si cleavage (eq. 3).

$$Cl_2MeSiSiMe_2Cl \xrightarrow{Pd^0} Me_2SiCl_2 + \text{polysilanes} \qquad (3)$$

In fact, dimethyldichlorosilane was produced in 20% yield during the addition reaction. Higher polysilanes also were produced, but the structures of the polysilanes were not determined in the present work.

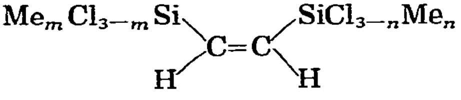
TABLE 2

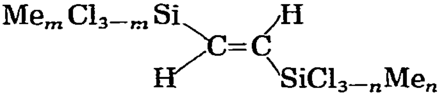
CHARACTERIZATION OF 1,2-BIS(CHLOROSILYL)ETHENES PREPARED

Compound	Stereo-chemistry	B.p. (°C/mmHg)	IR, principal absorptions (cm^{-1}) [a]	NMR δ (ppm) [b]	Analysis (found (calcd.) (%)) Hydrolyzable Cl
(*Z*)-I [10]			2970, 1405, 1335	1.02 (s, 6 H, SiMe)	
	79/21	57/2	1265, 630	6.94 (s, 2 H, =CH)	
(*E*)-I [10]			2970, 1405, 1266	0.91 (s, 6 H, SiMe)	
			1003	6.88 (s, 2 H, =CH)	
(*Z*)-II			2963, 1404, 1341	0.64 (s, 6 H, SiMe)	
			1260, 550	0.96 (s, 3 H, SiMe)	45.12
	80/20	73/8		6.82 (d, 1 H, =CH, *J* = 9 Hz)	(45.52)
				7.10 (d, 1 H, =CH, *J* = 9 Hz)	
(*E*)-II			2963, 1403, 1258	0.56 (s, 6 H, SiMe)	
			1003	0.87 (s, 3 H, SiMe)	
				6.59 (d, 1 H, =CH, *J* = 21 Hz)	
				7.02 (d, 1 H, =CH, *J* = 21 Hz)	
(*Z*)-III [10]			2955, 1402, 1340	0.50 (s, 12 H, SiMe)	
	89/11	69/6.5	1255, 580	6.85 (s, 2 H, =CH)	
(*E*)-III [10]			2955, 1405, 1255	0.51 (s, 12 H, SiMe)	
			1004	6.77 (s, 2 H, =CH)	
(*Z*)-IV			2950, 1402, 1340	0.18 (s, 9 H, SiMe)	
			1250, 560	0.52 (s, 6 H, SiMe)	
	93/7	79/32		6.71 (d, 1 H, =CH, *J* = 9 Hz)	17.66
				6.85 (d, 1 H, =CH, *J* = 9 Hz)	(18.38)
(*E*)-IV [9]			2956, 1407, 1248	0.10 (s, 9 H, SiMe)	
			1008	0.47 (s, 6 H, SiMe)	
				6.53 (d, 1 H, =CH, *J* = 22 Hz)	
				6.72 (d, 1 H, =CH, *J* = 22 Hz)	

[a] All spectra were taken with neat samples. [b] All spectra were taken in CCl_4 using Me_4Si as internal standard.

The palladium-catalyzed double silylation of substituted acetylenes shows (*Z*)-stereochemistry [1—4]. The present reaction also gave (*Z*)-products which were contaminated with 7—21% (*E*)-isomers. However, the formation of (*E*)-isomers may be attributed to the isomerization of (*Z*)-adducts during the course of the reactions. This explanation is supported by the fact that the amounts of (*E*)-isomers were found to increase as the reactions progressed. For example, in the addition of tetrachlorodimethyldisilane, the ratio of (*Z*)- to (*E*)-1,2-bis-(dichloromethylsilyl)ethene was 90/10 after 1 h; this ratio was 79/21 after 3 h. A control experiment disclosed that the (*Z*)-isomer isomerized significantly to the (*E*)-isomer in the presence of the palladium(0) complex and the starting chlorodisilane. Thus, heating a 72/28 mixture of the (*Z*)- and (*E*)-bis(silyl)-ethene at 80°C for 3 h in the presence of 1 mol% of the complex and the disilane (1 equiv.) gave a 56/44 mixture of the two isomers. The isomerization is reminiscent of the reported isomerization of (*Z*)-disilylated styrene derivatives promoted by the palladium(0) complex in the presence of methoxydisilanes [4].


(*Z*)-isomer


(*E*)-isomer

Several routes are now available to 1,2-bis(silyl)ethenes [6—10], but it should be noted that they gave only or mainly (*E*)-isomers. Published procedures for the convenient synthesis of (*Z*)-1,2-bis(silyl)ethenes are still lacking. It may be seen from Table 1 that the present double silylation provides a convenient route to (*Z*)-1,2-bis(chlorosilyl)ethenes. The starting chlorodisilanes are readily available [11], and the product chlorosilanes can be readily converted to many other derivatives such as alkyl-, alkoxy- and hydro-silanes etc.

Finally, catalyst efficiency was tested briefly for a palladium(II) complex, $PdCl_2(PPh_3)_2$, which has been shown to be an effective catalyst for the double silylation of acetylenes [2—4], using the addition of tetrachlorodimethyldisilane as a standard. It was thus found that the palladium(II) complex-catalyzed reaction gave only a 48% yield of a 70/30 mixture of (*Z*)- and (*E*)-1,2-bis(dichloromethylsilyl)ethene after heating at 80°C for 10 h.

Experimental

IR spectra were taken on a Hitachi EPI-3G spectrophotometer. NMR spectra were obtained with a Varian EM-360 spectrometer. GLC analyses were carried out with an Ohkura 802T instrument, using Teflon columns (100—150 × 0.4 cm) packed with Silicone KF-96, SE-30 and DCQF-1 on Celite 545 (60/80).

1,1,2,2-Tetrachloro-1,2-dimethyldisilane [11h], 1,1,2-trichloro-1,2,2-trimethyldisilane [11i], 1,2-dichloro-1,1,2,2-tetramethyldisilane [11i] and chloropentamethyldisilane [11d] were prepared according to published methods. Acetylene was commercially available and purified prior to use. The complexes $Pd(PPh_3)_4$ [12] and $PdCl_2(PPh_3)_2$ [13] were prepared by literature methods.

General procedure for the addition reactions

All reactions were conducted in an apparatus equipped with a reflux condenser, a magnetic stirrer, a thermometer and an inlet tube for acetylene gas.

A mixture of a chlorodisilane (5.00—6.84 g, 30 mmol), the palladium(0) complex (0.348 or 0.697 g, 0.30 or 0.60 mmol) and toluene or xylene (10 ml) was kept at 80—130°C for 3—11 h while acetylene gas was bubbled through the solution. Yields of 1,2-bis(chlorosilyl)ethenes produced were determined by GLC using an internal standard. Corrections were made for thermal conductivity of these products. For isolation of the products, the resulting mixtures were diluted with pentane, filtered, distilled under reduced pressure and subjected to preparative GLC.

Isomerization of 1,2-bis(dichloromethylsilyl)ethene in the presence of the palladium(0) complex and 1,1,2,2-tetrachloro-1,2-dimethyldisilane. A control experiment

A mixture of the bis(silyl)ethene ((*Z*)/(*E*) 72/28; 2.58 g, 10.2 mmol), the palladium(0) complex (0.120 g, 0.10 mmol), the disilane (2.23 g, 9.73 mmol) and toluene (8 ml) was heated at 80°C for 3 h. GLC and NMR analyses of the resulting mixture disclosed that the bis(silyl)ethene consisted of 56% (*Z*)- and 44% (*E*)-isomer.

References

1 Okinoshima, K. Yamamoto and M. Kumada, J. Organometal. Chem., 86 (1975) C27.

2 H. Sakurai, Y. Kamiyama and Y. Nakadaira, J. Am. Chem. Soc., 97 (1975) 931.

3 K. Tamao, T. Hayashi and M. Kumada, J. Organometal. Chem., 114 (1976) C19.

4 H. Watanabe, M. Kobayashi, K. Higuchi and Y. Nagai, J. Organometal. Chem., 186 (1980) 51.

5 H. Matsumoto, K. Shono, A. Wada, I. Matsubara, H. Watanabe and Y. Nagai, J. Organometal. Chem, in press.

6 H. Bock and H. Seidl, J. Organometal. Chem., 13 (1968) 87, and references cited therein.

7 J. Dunoguès, J.-P. Pillot, N. Duffaut and R. Calas, C.R. Akad. Sci. Ser. C278 (1974) 467.

8 D. Seyferth and S.C. Vick, J. Organometal. Chem., 144 (1978) 1.

9 L. Birkofer and T. Kühn, Chem. Ber., 111 (1978) 3119.

10 H. Matsumoto, S. Nagashima, T. Kato and Y. Nagai, Angew. Chem. Int. Ed. Engl. 17 (1978) 279.

11 (a) M. Kumada, M. Yamaguchi and M. Ishikawa, J. Org. Chem., 21 (1956) 1264; (b) M. Kumada and M. Ishikawa, J. Organometal. Chem., 1 (1963) 153; (c) M. Kumada, M. Ishikawa and S. Maeda, ibid., 2 (1968) 278; (d) H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, Tetrahedron Lett., (1966) 5497; (e) H. Sakurai, T. Watanabe and M. Kumada, J. Organometal. Chem., 7 (1967) P15; (f) E. Carberry, T. Keene and J. Johnson, J. Inorg. Nucl. Chem., 37 (1975) 839; (g) M. Ishikawa, M. Kumada and H. Sakurai, J. Organometal. Chem., 23 (1970) 63; (h) H. Watanabe, M. Kobayashi, Y. Koike, S. Nagashima, H. Matsumoto and Y. Nagai, ibid., 128 (1977) 173; (i) H. Matsumoto, T. Motegi, M. Hasegawa and Y. Nagai, ibid., 142 (1977) 149.

12 D.R. Coulson in F.A. Cotton (Ed.), "Inorganic Syntheses", Vol. XIII, McGraw-Hill, New York, 1972, p. 121.

13 J. Chatt and F.G. Mann, J. Chem. Soc., (1939) 1631.