Journal of Organometallic Chemistry, 195 (1980) 363—373

CONVENIENT LABORATORY SYNTHESIS OF VINYLIC SILICON COMPOUNDS VIA THE REACTIONS OF ACETYLENE WITH HYDROSILANES CATALYZED BY GROUP-VIII METAL PHOSPHINE COMPLEXES

Hamao Watanabe*, Muneo Asami and Yoichiro Nagai

Department of Chemistry, Gunma University, Kiryu, Gunma 376 (Japan)

(Received April 17th, 1980)

Summary

The hydrosilylation of acetylene (HC≡CH) with trichlorosilane, triethoxysilane, methyldichlorosilane, methyldiethoxysilane and n-hexyldichlorosilane in an inert solvent in the presence of various phosphine complexes of Group-VIII metals such as Ru, Rh, Pd and Pt, as well as chloroplatinic acid, was investigated. Among the complexes studied, $RuCl_2(PPh_3)_3$, $PtCl_2(PPh_3)_2$, $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$ and $Pt(PPh_3)_4$ were found to be the catalysts of choice for the selective syntheses of vinyltrichlorosilane, vinyltriethoxysilane, methylvinyldichlorosilane, methylvinyldiethoxysilane and n-hexylvinyldichlorosilane, respectively.

Introduction

Vinylic silicon compounds are versatile starting materials for various organosilicon derivatives and therefore much interest has been focused on their syntheses. Addition reactions of hydrosilanes to acetylene (HC≡CH) giving vinylsilanes catalyzed by chloroplatinic acid, platinum, palladium, base, phosphine or peroxide, have been studied extensively by many workers [1-3]. However, most of the reported catalytic hydrosilylations are not suitable for the laboratory synthesis of vinylic silicon compounds because these methods employed gas-phase flow-through systems or a high-pressure autoclave at an elevated temperature. Moreover, these methods often gave doubly silylated ethane derivatives rather than vinylsilanes. Therefore, it was desirable to find a simpler and more convenient method for acetylene hydrosilylation as a route to vinylic silicon compounds.

In continuing interest of the addition reactions of acetylenic compounds with hydrosilanes [4], we have now investigated the synthesis of various vinylsilanes via the hydrosilylation of acetylene, which can be conducted under atmospheric pressure in an inert solvent using various Group-VIII metal complexes as catalysts. In this work hydrosilanes, such as trichlorosilane, triethoxysilane, methyldichlorosilane, methyldiethoxysilane and _n_-hexyldichlorosilane, were employed, and the five respective vinylsilanes were obtained in good yield under mild conditions. The present reaction provides a convenient and selective monohydrosilylation of acetylene.

Results and discussion

The reactions were carried out by bubbling gaseous acetylene through a xylene or benzene solution containing the hydrosilane (such as trichlorosilane, triethoxysilane, methyldichlorosilane, methyldiethoxysilane and _n_-hexyldichlorosilane) together with a transition metal catalyst. The catalytic activities of Group-VIII metal phosphine complexes, $RuCl_2(PPh_3)_3$, $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $Pt(PPh_3)_4$ and $PtCl_2(PPh_3)_2$, were examined for the reaction of eq. 1 and the results are summarized in Table 1.

$$HC{\equiv}CH \quad + \quad HSiRX_2 \quad \xrightarrow[\text{(solvent)}]{\text{Catalyst}} \quad CH_2{=}CHSiRX_2 \quad + \quad (X_2RSiCH_2)_2 \qquad (1)$$

(I) (II) (III)

Ia, IIa, IIIa: R=X=Cl Ib, IIb, IIIb: R=X=OEt

Ic, IIc, IIIc: R=Me; X=Cl Id, IId, IIId: R=Me; X=OEt

Ie, IIe, IIIe: $R=\underline{n}-C_6H_{13}$; X=Cl

Table 1.

HYDROSILYLATION OF ACETYLENE WITH HYDROSILANES CATALYZED BY METAL PHOSPHINE COMPLEXES[a]

Run	Hydro-silane (mmol)	Solvent (ml)	Conditions			Product and yield (%)[d,e]	
			Cat.[b] (mol%)[c]	Temp. (°C)	Time		
	(Ia)	Xylene				(IIa)	(IIIa)
1	50	30	A (0.5)	80	3	90	0
2	250	150[f]	" (")	r.t.[g]	2.5	..(85)[h]	0
3	50	30	B (")	75-80	10	45	11
4	"	"	C (")	70-100	6	50	12
5	"	"	D (")	130	10	0	0
6	"	"	E (")	90	3	54	15
7	250	150	H (0.05)	60	3	90	0
	(Ib)	Benzene				(IIb)	(IIIb)
8	50	30	A (0.5)	80-100	13	trace	trace
9	"	"	B (")	75	3	54(45)	10
10	"	"	C (")	80	7	65(52)	16
11	"	"	D (")	"	5	74(63)	5
12	"	"	E (")	"	10	97(86)	3
13	"	"	F (")	110	15	0	0
14	"	"	G (")	"	"	0	0
15	"	"	H (0.05)	40	1	42(36)	37(30)
	(Ic)	Xylene				(IIc)	(IIIc)
16	50	30	A (0.5)	65	6	28	5
17	"	"	B (")	60-70	10	49	12
18	250	150[f]	" (")	84	14	46(40)	18(8)
19	50	30	C (")	55	3	54(44)	17(8)
20	"	"	D (")	70-80	11	45	23
21	"	"	E (")	72	7	12	36
22	"	"	G (")	70-80	3	30	40
23	"	"	H (0.05)	r.t.[g]	0.5	8	80

Table 1. Continued.

	(Id)	Benzene				(IId)	(IIId)
24	10	8	A (0.5)	80	7	8	trace
25	"	"	B (")	50	2	47	..(19)
26	"	"	C (")	r.t.[g]	1	80	18
27	200	150	" (")	"	2	..(89)	0
28	10	8	D (")	60	6	38	0
29	"	"	E (")	70	8	23	0
30	"	"	F (")	80-100	7	19	21
31	"	"	G (")	"	9	24	23
32	"	"	H (0.05)	r.t.[g]	1	5	78
33	200	150	" (")	"	2	0	..(80)
	(Ie)	Benzene				(IIe)	(IIIe)
34	20	13	A (0.5)	70	10	31	30
35	60	38	B (")	80	5	..(48)	22
36	20	13	C (")	60	10	49	27
37	40	30	D (")	80	2	87(78)	3
38	100	70	" (")	"	5	..(80)	trace
39	20	13	E (")	70-80	4.5	5	53
40	"	"	F (")	90	5	42	4
41	100	70	G (")	80-90	"	..(55)	5
42	40	30	H (0.05)	r.t.[g]	1	trace	82(76)

[a] A mixture of hydrosilane, catalyst and solvent was bubbled with acetylene gas. [b] A:$RuCl_2(PPh_3)_3$, B:$RhCl(PPh_3)_3$, C:$RhH(PPh_3)_4$, D:$Pt(PPh_3)_4$, E: $PtCl_2(PPh_3)_2$, F:$Pd(PPh_3)_4$, G:$PdCl_2(PPh_3)_2$, H:$H_2PtCl_6 \cdot 6H_2O$ in _i_-PrOH. [c] Relative to the hydrosilane used. [d] GLC yield based on the hydrosilane used. [e] Isolated yield in parenthesis. [f] Benzene solvent. [g] Exothermic reaction occurred. [h] Isolated as $CH_2{=}CHSi(OEt)_3$.

It will be seen from Table 1 that in the hydrosilylations using trichlorosilane to form vinyltrichlorosilane, all the phosphine complexes, except for $Pt(PPh_3)_4$ (Run 5), were catalytically effective. A ruthenium(II) complex, $RuCl_2(PPh_3)_3$, was shown to be the best catalyst. It gave IIa selectively and in good yield even at room temperature (Run 2), while two rhodium(I) complexes (Run 3 and 4) and $PtCl_2(PPh_3)_2$ (Run 6) afforded IIa only in 45-54% yield, accompanied by the formation of considerable amount of 1,2-bis(trichlorosilyl)ethane (IIIa) (11-15%).

Chloroplatinic acid-catalyzed reactions also gave IIa in good yield (Run 7), but the reactions required heating to occur. Because of the ease with which the ruthenium complex-catalyzed reaction can be conducted, the hydrosilylation by this catalyst in benzene solution was carried out in a preparative experiment and the result was quite satisfactory (Run 2). It should be noted that the present acetylene hydrosilylation affords the best yield (90%) for vinyltrichlorosilane among the reactions hitherto reported.

For the hydrosilylation with triethoxysilane, two rhodium(I) (Run 9 and 10) and two platinum (Run 11 and 12) complexes were effective catalysts, while ruthenium(II) (Run 8) and two palladium (Run 13 and 14) complexes were ineffective. The most selective and best catalyst was the platinum(II) complex, $PtCl_2(PPh_3)_2$, which afforded vinyltriethoxysilane (IIb) in nearly quantitative yield (Run 12). On the other hand, the chloroplatinic acid-catalyzed reaction gave only a mixture of IIb and 1,2-bis(triethoxysilyl)-ethane (IIIb) (Run 15).

The complexes described above also were effective catalysts of the hydrosilylation of acetylene with methyldichlorosilane. However, as seen in Table 1 (Run 16-22), these reactions always resulted in the formation of a mixture of methylvinyldichlorosilane (IIc) and 1,2-bis(methyldichlorosilyl)ethane (IIIc). Nevertheless, the reactions catalyzed by two rhodium(I) complexes, $RhCl(PPh_3)_3$ and $RhH(PPh_3)_4$ (Run 17-19), were satisfactory because the yields are moderate (49-54%), and the vinylsilane (IIc) could be easily separated from IIIc by fractional distillation. On the other hand, the chloroplatinic acid-catalyzed reaction was found to give IIIc almost exclusively (Run 23).

Similarly, the hydrosilylations with methyldiethoxysilane catalyzed by the rhodium and platinum complexes afforded methylvinyldiethoxysilane (IId) (Run 25-29). As seen in Table 1, the $RhH(PPh_3)_4$-catalyzed reaction gave good yields under mild conditions

(Run 26 and 27). The other reactions gave IId in low yields and the main product was the doubly silylated ethane (IIId). It is worthwhile to note that this is the first example of the mono-addition of methyldiethoxysilane to acetylene.

The reaction of n-hexyldichlorosilane with acetylene to give n-hexylvinyldichlorosilane (IIe) also was effected successfully in the presence of the phosphine complexes, giving moderate to good yields. $Pt(PPh_3)_4$ was the catalyst of choice for this particular hydrosilylation (Run 37 and 38). In contrast, platinum complexes such as $PtCl_2(PPh_3)_2$ and H_2PtCl_6 gave 1,2-bis(n-hexyldichlorosilyl)-ethane (IIIe) almost exclusively (Run 39 and 42).

The literature shows that the addition of hydrosilanes to vinylsilanes usually occurs very easily to form disilylethanes [1b] so that successful monohydrosilylation of acetylene by judicious choice of catalyst, as exemplified in the present work, opens a way to the convenient laboratory synthesis of a variety of vinylic silicon compounds under mild conditions.

Experimental

All boiling points are uncorrected. NMR spectra were measured on a Varian A-60D spectrometer in CCl_4, and IR spectra were recorded using neat liquid films with a Hitachi EPI-G3 spectrometer. GLC analyses were conducted using Ohkura Model 802 and 1700 gas chromatographs equipped with 2m × 3 mm or 4 mm Teflon column packed with Silicone SF-96 20% on Celite 545-AW (column temp. 150-190 °C; He carrier; an external standard, n-alkane in carbon chain C_8-C_{16}).

Materials

Trichloro-, triethoxy-, methyldichloro- and methyldiethoxysilane were commercially available. n-Hexyldichlorosilane was prepared by the previous method [5]. Acetylene gas was commercially available and was purified by passing it a Dry-Ice acetone trap and then a calcium chloride drying tube. Metal triphenylphosphine complexes, $RuCl_2(PPh_3)_3$ [6], $RhH(PPh_3)_4$ [7], $RhCl(PPh_3)_3$ [8], $Pd(PPh_3)_4$ [9], $PdCl_2(PPh_3)_2$ [10], $Pt(PPh_3)_4$ [11] and $PtCl_2(PPh_3)_2$ [10b] were obtained by literature methods. Chloroplatinic acid catalyst was obtained by dissolving $H_2PtCl_6 \cdot 6H_2O$ (1.0 g) in *i*-PrOH (10 ml).

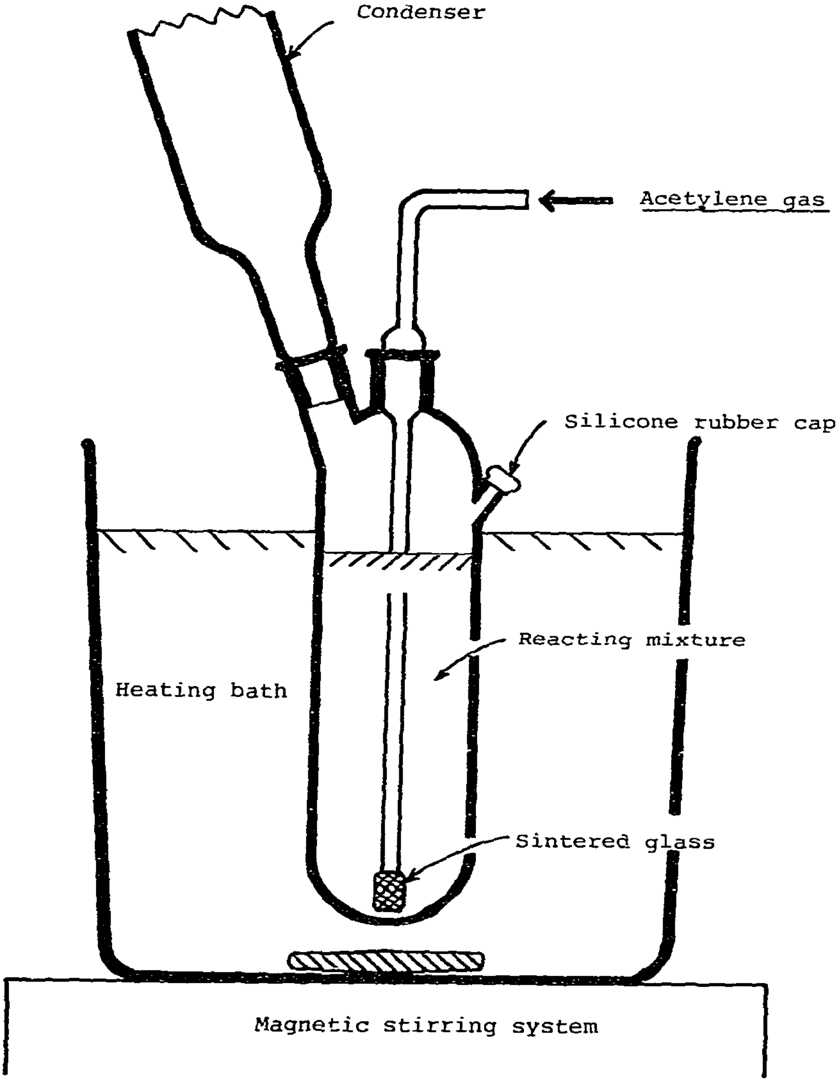

Fig. 1. Apparatus for the hydrosilylation of acetylene.

Syntheses of vinylic silicon compounds, IIa-IIe, via the hydrosilylations of acetylene with hydrosilanes, Ia-Ie

Vinyltrichlorosilane (IIa): A solution of trichlorosilane (Ia, 6.8 g, 50 mmol) in xylene (50 ml) and $RuCl_2(PPh_3)_3$ (0.240 g, 0.25 mmol; 0.5 mol% relative to $HSiCl_3$ used) were placed in a 80-ml specially devised thimble-shaped three-necked flask, equipped with a Dry-Ice acetone condenser the outlet of which was protected by a calcium chloride drying tube and with a gas-inlet tube the end of which was extended into the liquid nearly to the bottom of the flask. (Fig. 1). To this solution, acetylene gas was bubbled through the gas-inlet tube at 80 °C (oil bath) for 3 h. GLC analysis of the reaction mixture showed that vinyltrichlorosilane (IIa) had been formed in 90% yield, but that no 1,2-bis(trichlorosilyl)ethane (IIIb) was present (Table 1, Run 1).

In a preparative experiment using Ia (34 g, 0.25 mol), benzene (150 ml), $RuCl_2(PPh_3)_3$ (1.199 g, 1.25 mmol) and acetylene gas, a similar reaction was carried out without heating. An exothermic reaction occurred and Ia was consumed within 2.5 h. To make the separation of the product easier, the product (IIa) in the reaction mixture was converted into vinyltriethoxysilane (IIb) by refluxing it with ethanol (46 g, 1.0 mol) for 2 h. Distillation of the resulting mixture gave IIb, b.p. 156°; 39 g (85%); n_D^{25} 1.3962 (lit., b.p. 158°; n_D^{25} 1.3960 [12]) (Run 2). The NMR and IR spectra of the sample were superimposable with those of an authentic sample.

Vinyltriethoxysilane (IIb): In a similar manner to the above, except for the use of a Dimroth condenser in place of a Dry-Ice acetone condenser, acetylene gas was introduced into a solution containing Ib (8.2 g, 50 mmol) and $PtCl_2(PPh_3)_2$ (0.198 g, 0.25 mmol) in benzene (30 ml) at 80° for 10 h. GLC anlaysis of the reaction mixture showed that vinyltriethoxysilane (IIb) and 1,2-bis(triethoxysilyl)ethane (IIIb) had been formded in yields of 97 and 3%, respectively (Run 12). After evaporation of the solvent, the mixture was distilled to give IIb, 8.2 g (86%); b.p. 78-80°/90 mmHg.

Methylvinyldichlorosilane (IIc): A solution of Ic (28.8 g, 0.25 mol) and $RhCl(PPh_3)_3$ (1.157 g, 1.25 mmol) in xylene (150 ml) was treated similarly with acetylene at 84° for 14 h. Upon distillation, the reaction mixture gave IIc, 14.1 g (40%); b.p. 90-91°; n_D^{20} 1.0856 (lit., b.p. 91°; n_D^{20} 1.0863 [13]) and IIIc, 1.6 g (8%); b.p. 113-115°/50 mmHg; n_D^{20} 1.4758 (lit., b.p. 72°/9 mmHg [14]) (Run 18).

Methylvinyldiethoxysilane (IId): Into a solution of Id (26.9 g, 0.2 mol) and $RhH(PPh_3)_4$ in benzene (150 ml) was bubbled acetylene for 2 h without heating (Run 27). Distillation of the mixture afforded IId, 28.6 g (89%); b.p. 132-134°; n_D^{25} 1.4087 (lit., b.p. 133-134°; n_D^{25} 1.4091 [12]).

A similar reaction of Id (0.2 mol) with acetylene in the presence of chloroplatinic acid (0.1 mmol; 1.04 ml of the *i*-PrOH solution) (Run 33) gave, after distillation, 1,2-bis(methyldiethoxysilyl)ethane (IIId), 23.5 g (80%); b.p. 118-120°/2 mmHg; n_D^{20} 1.4145; $[C\underset{a}{\underline{H}}_3(C\underset{b}{\underline{H}}_3C\underset{c}{\underline{H}}_2O)_2SiC\underset{d}{\underline{H}}_2]_2$; Found: C, 48.78; H, 9.88%, Calcd. for $C_{12}H_{30}Si_2O_4$: C, 48.84; H, 10.27%; NMR (CCl_4, TMS) (δ, ppm): 3.72 (q, H_c, 8H), 1.20 (t, H_b, 12H), 0.45 (s, H_d, 4H), 0.01 (s, H_a, 6H); IR (neat, sandwich) (cm^{-1}): 2980, 2920, 2890 (νCH); 1100, 1050 (Si-O-C); 1250 (Si-Me).

n-Hexylvinyldichlorosilane (IIe): Likewise, acetylene was introduced into a solution of *n*-hexyldichlorosilane (18.5 g, 0.1 mol) and $Pt(PPh_3)_4$ (0.622 g, 0.5 mmol) in benzene (70 ml) at 80° for 5 h, giving 15.3 g (80%) of IIe, b.p. 113-115°/51 mmHg (Run 38).

However, the product formed in a similar reaction using chloroplatinic acid catalyst was only 1,2-bis(*n*-hexyldichlorosilyl)ethane (IIIe); b.p. 159-161°/2 mmHg; 76% (Run 42).

The analytical and physical data of the two products are as follows: (IIe) $n\text{-}C_6\underset{a}{\underline{H}}_{13}SiCl_2(C\underset{b}{\underline{H}}=C\underset{b}{\underline{H}}_2)$; Found: C, 45.59; H, 7.65%, Calcd. for $C_8H_{16}SiCl_2$: C, 45.49; H, 7.64%; NMR (CCl_4, TMS) (δ, ppm): 6.16 (s, H_b, 3H), 1.84-0.66 (m, H_a, 13H); IR (neat, sandwich) (cm^{-1});

3050 (=CH_2); 3010 (=CH-); 2940, 2910, 2850 (νCH), and (IIIe) (*n*-$C_6\underline{H}_{a}{}_{13}SiCl_2C\underline{H}_{b}{}_2)_2$; Found: C, 42.83; H, 7.46%, Calcd. for $C_{14}H_{30}Cl_4Si_2$: C, 42.42; H, 7.63%; NMR (CCl_4, TMS) (δ, ppm); 1.18 (s, H_b), 1.80-0.66 (m, H_a); IR (neat, sandwich) (cm^{-1}): 2940, 2910, 2850 (νCH); 1465, 1400, 1150.

References

1 (a) C. Eaborn, "Organosilicon Compounds", Butterworths Scientific Publications, London, 1960, p. 55; (b) C. Eaborn and R. W. Bott, "Organometallic Compounds of the Group IV Elements" Vol. 1, The Bond to Carbon, Part II, Marcel Dekker, Inc., New York, 1968, p. 269, and the literatures cited therein; (c) E. Lukevics and M. Voronkov, "Organic Insertion Reactions of Group IV Elements", Consultants Bureau, New York, 1966, p. 65; (d) E. Lukevics, Z. Belyakova, M. Pomerantseva and M. Voronkov, J. Organometal. Chem., Library 5, 1977, p. 61.

2 M. Kraus, Z. Zitny, O. Kruchna and J. Rathousky, Czech. Pat. 164,156 (1976); Chem. Abstr., 86 (1977) 140237h.

3 (a) M. Kraus, Coll. Czech. Chem. Comm., 39 (1974) 1318; (b) M. Mejstrikova, M. Kraus, Czech. Pat. 164,584 (1976); Chem. Abstr., 86 (1977) 141262z.

4 H. Watanabe, T. Kitahara, T. Motegi and Y. Nagai, J. Organometal. Chem., 139 (1977) 215.

5 H. Watanabe, M. Aoki, N. Sakurai, K. Watanabe and Y. Nagai, J. Organometal. Chem., 160 (1978) C1.

6 P. S. Hallman, T. A. Stephenson and G. Wilkinson, Inorg. Syn., XII (1970) 238.

7 N. Ahmad, J. J. Levison, S. D. Robinson and M. F. Uttley, Inorg. Syn., XV (1974) 58.

8 J. A. Osborn and G. Wilkinson, Inorg. Syn., X (1967) 67.

9 D. R. Coulson, Inorg. Syn., XIII (1972) 121.

10 (a)F. G. Mann and D. Purdie, J. Chem. Soc., Part III, (1953) 1549;(b)F. R. Hartley, Organometal. Chem. Rev., A, 6 (1970) 119.

11 R. Ugo, F. Cariati and G. La Monica, Inorg. Syn., XI (1968) 105.

12 M. Cohen and J. R. Ladd., J. Amer. Chem. Soc., 75 (1953) 988.

13 M. F. Shostakovskii and D. A. Kochkin, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, (1956) 967;Chem. Abstr., 51 (1957) 4983.

14 M. F. Shostakovskii and D. A. Kochkin, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, (1956) 632;Chem. Abstr., 51 (1957) 1026.