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DEHYDROCONDENSATION OF TRIALKYLSILANES WITH ACETYLENE AND MONOSUBSTITUTED ACETYLENES *

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Summary

Trialkylsilanes readily undergo dehydrocondensation with acetylene and substituted acetylenes in the presence of the catalytic systems, H_2PtCl_6/iodine, lithium iodide or /trialkyliodosilanes, and so the monosubstituted acetylenes $HC{\equiv}CR$ ($R = C_4H_9$, $C(CH_3)_3$, CH_2Cl, C_6H_5) smoothly afford the corresponding trialkyl(organylethynyl)silanes. In hexane or benzene the yield of the dehydrocondensation products amounts to 90%. The products of the dehydrocondensation of triethylsilane with acetylene are bis(triethylsilyl)acetylene and 1,2-bis(triethylsilyl)ethane. The reaction mechanism is discussed.

Introduction

The well-known reaction of trialkylsilanes with acetylene and monosubstituted acetylenes leads to mono- and di-adducts, i.e., the hydrosilylation reaction takes place [1–3].

The study of the promotion of platinum catalysts in the hydrosilylation of acetylenic compounds [4] has established that the addition to $H_2PtCl_6 \cdot 6H_2O$ of lithium iodide (molar ratio, 1 : 100–1 : 200) sharply changes the course of the reaction [5]. In the presence of this catalytic system, triethylsilane reacts with monosubstituted acetylenes to form, predominantly, the dehydrocondensation product (eq. 1).

$$Et_3SiH + HC{\equiv}CR \rightarrow Et_3SiC{\equiv}CR + H_2 \qquad (1)$$

Trialkylethynylsilane and trialkyl(organylethynyl)silanes, obtained in this way directly from acetylene and its monosubstituted derivatives, have been prepared earlier but with difficulty. Compounds of this series are formed in low yield (not

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* Dedicated to Professor Raymond Calas on the occasion of his 70th birthday in recognition of his outstanding research in organometallic chemistry during more than 30 years.

higher than 15%) by the reaction of trimethylchlorosilanes with monosubstituted acetylenes in the presence of Li, Na or Mg in THF or HMPA at elevated temperature and pressure [6–12]. 1,2-Bis(trimethylsilyl)ethylene (30% yield) is the main product of the reaction of trimethylchlorosilane with phenylacetylene [12].

In the reaction of monosubstituted acetylenes HC≡CR ($R = C_4H_9$, C_6H_5) with trimethyliodosilane in the presence of metallic Mg at 170–180°C the yields of the corresponding trimethyl(organylethynyl)silanes are 80–95% [13].

$$Me_3SiI + HC{\equiv}CR \xrightarrow[-HI]{Mg} Me_3SiC{\equiv}CR \qquad (2)$$

Developing the research outlined in a preliminary communication [5] we have investigated in detail the dehydrocondensation of trialkylsilanes, using the reaction of triethyl- and trimethyl-silanes with acetylene and its monosubstituted derivatives.

Results and discussion

In the course of investigation of the H_2PtCl_6 promotion with metal halides we have established that lithium iodide is the most efficient catalyst for the dehydrocondensation of trialkylsilanes with monosubstituted acetylenes, which proceeds according to eq. 1. The replacement of the iodide by chloride or bromide, or by the iodide of another alkali metal, or by zinc, aluminium or nickel iodide, i.e., a change in the anion or cation, decreases the catalytic activity of the system in this reaction (Table 1). The addition of LiI_3 to H_2PtCl_6 is more effective than the use of LiI. Further, it has been found that elemental iodine is an even more effective additive.

Remarkable results have been obtained with trimethyl- or triethyl-iodosilane (the product of the reaction of iodine with the corresponding trialkylsilane [14]) as the activating additive. Here the hydrosilylation is almost completely inhibited, the yield of the product of the dehydrocondensation of triethylsilane with phenylacetylene reaching 93%. In the reaction of triethylsilane with butylacetylene in the presence of

TABLE 1

EFFECT OF THE SYSTEM H_2PtCl_6–HALIDE (1:100) ON THE PRODUCT YIELD IN THE REACTION OF TRIETHYLSILANE WITH PHENYLACETYLENE IN HEXANE, $T = 20°C$

Halide	Yield (%)		
	$Et_3SiC{\equiv}CPh$	$Et_3SiCH{=}CHPh$	$Et_3SiC({=}CH_2)Ph$
LiCl	0	84.4	15.6
LiBr	4.1	79.3	16.6
LiI	72.7	15.1	12.2
LiI_3	79.1	11.2	9.7
NaI	41.3	47.4	11.3
KI	20.0	66.8	13.2
ZnI_2	0	76.1	23.9
$AlCl_3$	0	74.2	25.8
AlI_3	62.1	19.4	18.5
I_2	82.9	9.2	7.9
NiI_2	27.0	40.1	32.9
Me_3SiI	92.1	6.0	1.9
Et_3SiI	93.4	5.8	trace

the H_2PtCl_6–Et_3SiI system (in molar ratios of 1 : 100 and 1 : 200) the yield of triethyl(butylethynyl)silane is as high as 92%.

When Et_3SiI is added to H_2PtCl_6, the conversion of the starting reagents is very high (about 90%) and the dehydrocondensation is completed during 1–2 h. Nevertheless, in the search for the optimum conditions for the dehydrocondensation of acetylene and monosubstituted acetylenes with trialkylsilanes, we have used mainly the catalytic system H_2PtCl_6/I_2, which is equivalent to the *in situ* system H_2PtCl_6/R_3SiI.

We have established that various monosubstituted acetylenes $HC{\equiv}CR$ react with triethylsilane in the presence of a binary catalytic system, H_2PtCl/LiI or H_2PtCl_6/I_2, in hexane at temperatures as low as 20°C to form the corresponding triethyl(organylethynyl)silanes in high yields (80–90%) (Table 2). The data in Table 2 show that the substituent R in the $HC{\equiv}CR$ molecule does not have much effect on the final yield of the dehydrocondensation product in spite of different relative CH acidities of the starting acetylenic compounds [15].

The dehydrocondensation with monosubstituted acetylenes may also occur with other trialkylsilanes. Thus, for example, in the presence of the H_2PtCl_6/I_2 system under the conditions used for the study, trimethylsilane reacts with 1-hexyne and with phenylacetylene to form the corresponding trimethyl(organylethynyl)silanes in 68% and 34% yield, respectively (see Table 2). The side reaction of hydrosilylation proceeds to a small extent in this case. The total yield of the mono-adducts, $Et_3SiC(=CH_2)R$ and *trans*-$Et_3SiCH{=}CHR$, does not exceed 15%, their ratio being approximately 1 : 1. However, the dehydrocondensation/hydrosilylation ratio depends greatly on the reaction temperature. Thus, the reaction of triethylsilane with phenylacetylene in benzene in the presence of the H_2PtCl_6–I_2 system at temperature above 60°C affords only the hydrosilylation products. Under analogous conditions but at 40 and 20°C the ratios of $Et_3SiC{\equiv}CPh : Et_3SiC(=CH_2)Ph : Et_3SiCH{=}CHPh$ are 37.4 : 16.7 : 35.5 and 63.0 : 10.9 : 7.2, respectively.

The dehydrocondensation of triethylsilane with monosubstituted acetylenes should be carried out under conditions providing for the removal of the hydrogen formed, otherwise the reaction is followed by hydrogenation of the triethyl(organylethynyl)silane to give *cis*-triethyl(organylvinyl)silane in yields of 10–15%.

$$Et_3SiC{\equiv}CR + H_2 \rightarrow cis\text{-}Et_3SiCH{=}CHR \qquad (3)$$

The dehydrocondensation/hydrosilylation ratio is also affected greatly by the solvent used. As shown in Table 3, the maximum yield of the dehydrocondensation product is observed in aliphatic (hexane) or aromatic (benzene, *o*-xylene) hydrocarbons. Polar electron-donor solvents (THF, acetonitrile) greatly inhibit the dehydrocondensation (eq. 1), which at first sight seems unexpected, since these solvents increase the acidity of the acetylenic hydrogen (due to hydrogen bond formation [15]) and the hydride character of the hydrogen atom attached to silicon (due to the Si-atom coordination [16]).

The inhibition of the dehydrocondensation in THF and CH_3CN may be explained by the formation of charge transfer complexes of the type $I_2^- \ldots S^+$ with either iodine [17] or the platinum catalyst [18]. With increasing solvent polarity the conversion of the starting reagent drops as well.

The dehydrocondensation of triethylsilane with acetylene under analogous conditions leads to bis(triethylsilyl)acetylene and 1,2-bis(triethylsilyl)ethane in a 4 : 1 ratio.

TABLE 2

PRODUCTS OF THE REACTION OF TRIALKYLSILANES WITH ACETYLENE AND MONOSUBSTITUTED ACETYLENES $R_3SiC{\equiv}CR'$ (2 h, 20°C, HEXANE, H_2PtCl_6/I_2: LiI = 1 : 100)

R	R′	Promoter	Yield (%) [a]	B.p. (°C/mm Hg)	Analysis: Found(Calcd.) (%)			
					C	H	Si	Cl
Et_3 [b]	Et_3	I_2	24	125–127/12	65.75	11.96	22.29	
					(66.05)	(11.87)	(22.06)	
Et_3 [c]	Bu	I_2	96	111–112/25	73.27	12.34	!4.39	
					(73.38)	(12.32)	(14.30)	
Et_3	t-Bu	I_2	86	78–79/15	73.42	12.29	14.29	
					(73.38)	(12.32)	(14.30)	
Et_3 [d]	Ph	I_2	89	102–104/1	77.84	9.40	12.76	
					(77.70)	(9.32)	(12.98)	
Et_3 [e]	CH_2Cl	LiI	74	80–82/8	64.10	9.71	14.80	17.94
					(67.26)	(9.08)	(14.88)	(18.78)
Me_3	Bu	I_2	68	63–64/30	70.31	11.72	17.97	
					(70.04)	(11.76)	(18.20)	
Me_3 [f]	Ph	I_2	34	59–61/1	75.32	8.31	16.37	
					(75.79)	(8.10)	(16.11)	

[a] from GLC. [b] n_D^{20} 1.4570. [c] n_D^{20} 1.4490, d_4^{20} 0.8069, [d] n_D^{20} 1.5288, d_4^{20} 0.8990. [e] n_D^{20} 1.4681, d_4^{20} 0.9211. [f] n_D^{20} 1.5240.

TABLE 3

EFFECT OF SOLVENT ON THE COURSE OF THE REACTION OF TRIETHYLSILANE WITH PHENYLACETYLENE AT 20°C WITH THE CATALYTIC SYSTEM, $H_2PtCl_6:I_2$ (1:100)

Solvent	Yield (%) [a]		
	$Et_3SiC{\equiv}CPh$	$Et_3SiC({=}CH_2)Ph$	$Et_3SiCH{=}CHPh$
Hexane	82.9	11.6	5.5
Benzene	73.5	19.0	5.4
o-Xylene	54.4	36.7	1.3
THF	36.7	53.5	3.3
Acetonitrile	22.3	6.5	71.2

[a] From GLC data.

The latter is most likely to be the product of acetylene hydrosilylation [19]. The formation of 1,2-bis(triethylsilyl)ethane by hydrogenation of bis(triethylsilyl)acetylene (eq. 4) with the liberated hydrogen is less probable.

$$2\ Et_3SiH + HC{\equiv}CH \rightarrow Et_3SiCH_2CH_2SiEt_3 \qquad (4)$$

The structures of all the compounds obtained (Table 2) have been confirmed by ^1H and ^{13}C NMR, and IR spectroscopy (Table 4), gas chromatography/mass spectrometry (Table 5) and GLC (in comparison with standards).

Unlike trialkylsilanes, hydrosilylating agents of the type $R_{3-n}X_nSi{-}H$ ($n = 2,3$), containing the electron-withdrawing substitutent X (X = Cl, EtO) at the silicon atom, reluctantly enter into dehydrocondensation with monosubstituted acetylenes or fail to react in this way (Table 6).

The data in Tables 2 and 6 show that the reactivity of $R_{3-n}X_nSiH$ compounds towards dehydrocondensation with monosubstituted acetylenes increases with in-

TABLE 4

IR AND ^1H, ^{13}C NMR SPECTRAL DATA FOR THE REACTION PRODUCTS FROM TRIETHYLSILANE AND ACETYLENE OR MONOSUBSTITUTED ACETYLENES

Starting acetylene	IR, C≡C (cm^{-1})	NMR δ (ppm)	
		^1H	^{13}C
$HC{\equiv}CH$	2110 (s)	0.91, 0.93 (CH_3) 0.39, 0.50 (CH_2Si)	6.94 (CH_3), 4.66 (CH_2Si), 61.49 (≡C)
$HC{\equiv}CBu$	2180 (s)	5.25, 5.59 (=CH_2), 5.48 (=CHSi) 5.98 (=CH)	
$HC{\equiv}CBu$-tert	2155 (s) 2190 (m)	5.31, 5.76 (=CH_2) 5.35 (=CHSi) 5.96 (=CH)	
$HC{\equiv}CPh$	2160 (s)	5.53, 5.83 (=CH_2) 6.33 (=CHSi) 6.81 (=CH)	
$HC{\equiv}CCH_2Cl$	2180 (s)	0.93 (CH_3) 0.50 (CH_2Si) 4.13 (CH_2Cl) 5.74, 6.05 (HC=CH)	7.43 (CH_3), 3.47, 4.39 (CH_2Si), 30.29, 46.81 48.76 (CH_2Cl), 130.51, 144.27 (=SiC), 101.09 (≡C) 89.07 (≡SiC)

TABLE 5

MASS SPECTRA OF THE REACTION PRODUCTS FROM $Et_3SiC{\equiv}CR$

m/e (rel.int.) assignment	R = Bu	k = Ph	R = CH_2Cl
M^+	196 (6.2)	216 (13.2)	188 (4.9)
M^+-Et	167 (100)	187 (100	159 (100)
M^+-Et-C_2H_4	139 (71.9)	159 (90.5)	131 (28.8)
M^+-Et-$2C_2H_4$	111 (39.6)	131 (82.1)	103 (28.8)
PhC_2H_2		21.4	
M^+-Vinyl			161 (25.0)
M^+-Vinyl-C_2H_4			133 (28.8)
M^+-Vinyl-$2C_2H_4$			105 (14.4)
Et_2SiCl			121 (9.9)

crease in the total +I-effect of the substituents on the silicon atom, i.e., with increase in the hydride character of the hydrogen atom attached to silicon (cf. [3]).

Taking into consideration the fact that monosubstituted acetylenes are CH-acids (on the polarographic scale, the pK_a value for $PhC{\equiv}CH$ is 18.5 [20]) we have examined the possibility of dehydrocondensation of triethylsilane with other CH acids, such as chloroform, acetonitrile, malononitrile, acetylacetone, acetophenone, containing a mobile hydrogen atom which can be substituted by metal. It turned out, however, that under the optimum conditions for acetylenes, these CH acids fail to enter into the dehydrocondensation reaction. With chloroform, acetonitrile and malononitrile no hydrosilylation takes place either, whereas with acetophenone and acetylacetone, hydrosilylation of the carbonyl group occurs, to give $PhCHMeOSiEt_3$ and $CH_2(CHMeOSiEt_3)_2$ in up to 20% yield. This indicates that the H_2PtCl_6/I_2 system is not a universal catalyst for the dehydrocondensation of trialkylsilane with CH acids, being efficient only with acetylene and monosubstituted acetylenes.

The mechanism of the dehydrocondensation of trialkylsilanes with acetylene and its monosubstituted derivatives is far from simple.

Without H_2PtCl_2, the reaction of triethylsilane with monosubstituted acetylenes in the presence of I_2, LiI or Et_3SiI does not occur. With only H_2PtCl_6 no reaction takes place. This implies that both components of the catalytic system are of importance in the process of dehydrocondensation. At the same time, triethyliodosi-

TABLE 6

PRODUCT YIELDS IN THE REACTION OF $R_{3-n}X_nSiH$ WITH PHENYLACETYLENE (H_2PtCl_6-I_2, 20°C, HEXANE, FROM GLC DATA)

$R_{3-n}X_nSiH$	Yield (%)	
	$R_{3-n}X_nSiC{\equiv}CPh$	Total yield of the hydrosilylation products
$(EtO)_3SiH$	16.0	81.8
$EtSiHCl_2$	3.0	95
	0 [a]	
$HSiCl_3$	0	0
$(Me_3SiHO)_n$	0	0

[a] In the presence of LiI

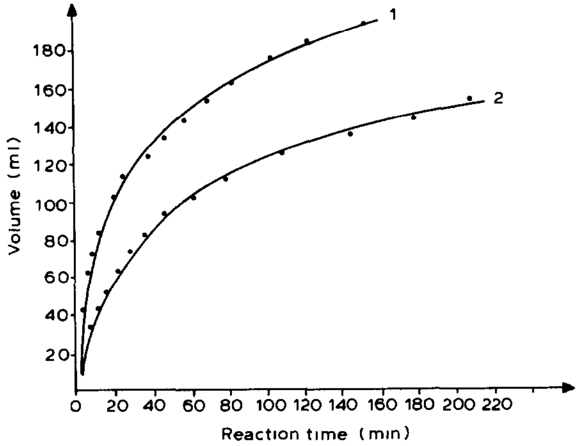

Fig. 1. Hydrogen evolved vs. reaction time in the dehydrocondensation of phenylacetylene (curve 1) and butylacetylene (curve 2) with triethylsilane in the presence of H_2PtCl_6/I_2.

lane in the presence of H_2PtCl_6 fails to react with monosubstituted acetylenes in the absence of triethylsilane under the conditions studied. Reaction of phenylacetylene with Me_3SiI and Et_3SiH (in the molar ratio 2 : 1 : 1) gives equi-molar amounts of triethyl(phenylethynyl)silane and trimethyl(phenylethynyl)silane.

Figures 1 and 2 show typical kinetic curves, illustrating the course of the dehydrocondensation of triethylsilane with butyl- and phenylacetylene. It is seen that the process has no induction period (similar to the catalyzed hydrosilylation of acetylenic compounds [21]) and that phenylacetylene reacts with triethylsilane 1.5 times as fast as with butylacetylene. The volume of the hydrogen evolved (Fig. 1) always conforms to the yield of the dehydrocondensation product (Fig. 2). This confirms that no side hydrogenation of triethyl(organylethynyl)silane with the liberated hydrogen occurs under the above conditions.

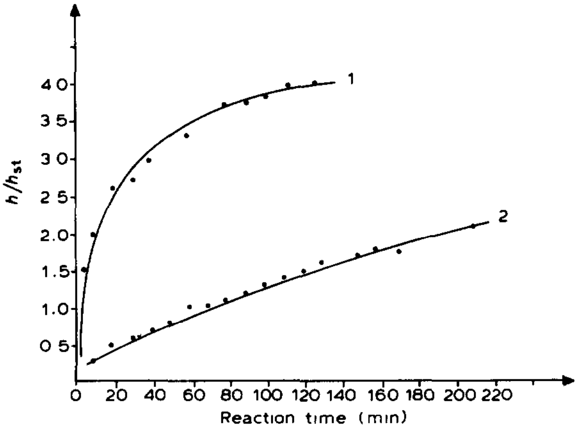

Fig. 2. Kinetic curves for the reaction of triethylsilane with phenylacetylene (curve 1) and butylacetylene (curve 2) in the presence of H_2PtCl_6/I_2 (h/h_{st} is the ratio of the area of the GLC peak for the product compared with that for the standard).

Since the pK_a values of butyl- and phenyl-acetylene are nearly equal [22] the higher dehydrocondensation rate of triethylsilane with phenylacetylene can be explained in terms of the carbanion $C_6H_5C{\equiv}C^-$ stabilization due to the triple bond-aromatic ring conjugation. We believe that the mechanism of dehydrocondensation of trialkylsilanes with acetylene and monosubstituted acetylenes may be represented by the following scheme:

$$R_3SiI + HC{\equiv}CR' \rightleftarrows R_3SiC{\equiv}CR' + HI \qquad (5)$$

$$R_3SiH + HI \rightarrow R_3SiI + H_2 \qquad (6)$$

The above equations indicate that the trialkylsilane functions as both the donor of trialkyliodosilane, directly condensed with an acetylene compound, and as the acceptor of the hydrogen iodide, removal of which is responsible for the displacement of the reaction (5) equilibrium to the right. The formation of trialkyliodosilane by the reaction of trialkylsilanes with iodine or hydrogen iodide has been described previously [14].

Triethyliodosilane is also the product of the reaction of triethylsilane with lithium iodide, which readily evolves free iodine in the presence of an oxidant such as H_2PtCl_6 [23]. The role of the latter (more exactly, the reduced form of H_2PtCl_6) evidently consists in the formation of an H_2PtCl_6/monosubstituted acetylene π-complex, facilitating the proton abstraction from the ethynyl group. The carbanion formed is attacked by the triethyliodosilane molecule, an efficient electrophilic agent.

All of the data obtained throw some light on the formation of dehydrocondensation side products in the course of hydrosilylation of monosubstituted acetylenes with trialkylsilanes, catalysed by Pt or Rh complexes containing iodine as a ligand [24].

Experimental

Measurements

The reaction mixtures obtained as described above were subjected to gas chromatographic analysis. This was performed on a Tsvett-102 instrument, equipped with a thermal conductivity detector (2 m column packed with 5% Lukopren on Chromaton AW), and using a programmed temperature (from 50 to 200°C). The ratio and yield of the reaction products were established from three parallel runs. The error in determining the relative contents does not exceed 1–1.5%.

IR spectra of 10% solutions of compounds in CCl_4 (most frequently) were recorded on an Ur-20 spectrometer in the 400–4000 cm^{-1} region.

^{1}H NMR spectra of (usually) 20–30% CCl_4 solutions of the compounds were taken on EX-90Q and Tesla-BS 487-C (80 MHz) spectrometers, with cyclohexane as the internal standard.

^{13}C NMR spectra were recorded on a Jeol-GX-90 spectrometer at 25°C for 20% CCl_4 solutions, with TMS as the internal standard.

Mass spectra were obtained on a MAT-212 chromatography-mass spectrometer at 70 eV, 20 m capillary column, phase SE-54, using a programmed temperature (5°C/min).

Materials

The starting acetylene compounds and hydrosilanes, $R_{3-n}X_nSiH$ ($n = 1$–3) were obtained and purified by conventional methods. The physical constants of these compounds were consistent with the most reliable literature data, the purity being within 99.5% according to GLC data.

Trialkyl(organylethynyl)silanes and trialkyl(organylvinyl)silanes used as standards in GLC were prepared and purified by published methods [25,26].

General procedures

The general procedure for the dehydrocondensation of trialkylsilanes with monosubstituted acetylenes is given for $C_6H_5C{\equiv}CH$ and $(C_2H_5)_3SiH$.

A mixture of 2.04 g (20 mmol) of $C_6H_5C{\equiv}CH$, 2.3 g (20 mmol) of $(C_2H_5)_3SiH$, 0.1 ml of a 0.05 *M* $H_2PtCl_6 \cdot 6H_2O$ solution in THF, 0.13 g of I_2 in 5.0 ml of hexane was kept at 20°C until hydrogen stopped evolving. The yield of $PhC{\equiv}CSiEt_3$, isolated by distillation, was 3.2 g (74%), b.p. 103°C (1 mmHg), n_D^{20} 1.5280, d_4^{20} 0.8970 [13]. From GLC, the hydrosilylation product content of the reaction mixture was approximately 9%.

Reaction of trialkylsilanes with monosubstituted acetylenes in the presence of the catalytic systems H_2PtCl_6 with LiI or with R_3SiI were performed in a similar manner.

A mixture of 4.6 g (40 mmol) of triethylsilane, 0.1 ml of a 0.05 *M* $H_2PtCl_6 \cdot 6H_2O$ solution in THF, and 0.13 g of I_2 was placed in a reaction vessel equipped with a gas-inlet tube, thermometer and a dry-ice acetone condenser cooled to −10°C. Acetylene gas was slowly bubbled into this solution through the gas tube at 20°C for 2 h. Distillation of the reaction mixture afforded 1 g (20%) of $Et_3SiC{\equiv}CSiEt_3$, b.p. 125–127°C (12 mmHg), n_D^{20} 1.4570.

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