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ORGANOCOPPER(I) MEDIATED SYNTHESIS OF 1-ALKENYLSILANES AND 1,3-ALKADIENYLSILANES FROM ETHYNYLSILANES

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Summary

Ethynylsilanes (I) are converted into α-silyl substituted (Z)-alkenylcopper(I) compounds (II) by treatment with RCu reagents. The adducts II react with a variety of electrophiles to give the 1-alkenylsilanes $RCH{=}C(E)SiR_3'$ (III: E = H, Cl, Br, I, CN, $SnMe_3$, SMe, Me, $H_2C{=}CHCH_2$). The conversion of I into III (E = H) can also be effected by using homocuprates, $R_2CuMgCl$, and triorganodicuprates, R_3Cu_2MgCl. The latter reagent should be used when the group R is methyl. An interesting 1,3-diene formation is observed on treating excess of ethynyltrimethylsilane (Ib) with R_3Cu_2MgCl; this reaction involves addition of intermediary vinylcuprates to unreacted 1-alkynylsilane (Ib). The intermediary 1,3-dienyl adduct (VIIb) reacts with various electrophiles to give 1,3-dienes, $RCH{=}C(SiMe_3)$-$CH{=}C(E)SiMe_3$ (VIIIb).

Introduction

The overwhelming number of reports on the use of organocopper(I) reagents shows that the reagents are excellent synthetic tools [1]. A very important property of the reagents is their ability to convert 1-alkynes into vinylcopper(I) species [2]; such a reaction provides an attractive entry into the synthesis of e.g., juvenile hormones [3].

Some time ago, we reported preliminary results on the successful addition of organocopper(I) compounds to ethynyltriphenylsilane [4]. A report appearing at the same time was concerned with ethynyltrimethylsilane [5]. The produced vinylsilanes are useful synthetic intermediates [6]. In this paper, a detailed study of the conversion of ethynylsilanes into vinylsilanes by organocopper(I) species is presented. It is shown that the choice of the organocopper(I) reagent may be crucial. Observation of an unexpected formation of a 1,3-diene is also discussed.

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Results and discussion

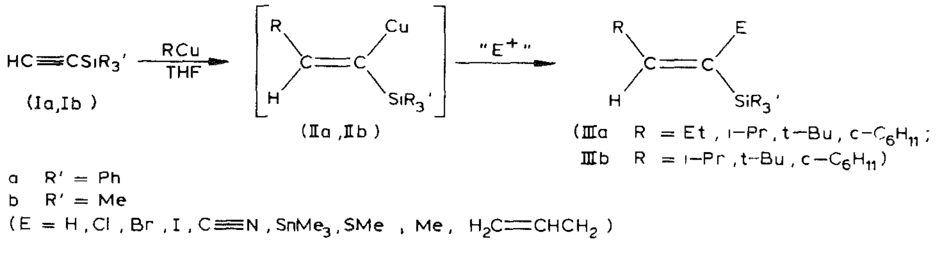
General remarks. In this investigation organocopper(I) species of the types RCu, $R_2CuMgCl$, and R_3Cu_2MgCl were used. These copper(I) species were obtained by adding the Grignard reagent RMgCl to appropriate amounts of $LiCuBr_2$ (solvent, THF) at $-60\,^\circ C$ and stirring the resulting mixtures for 0.5 h at $-60\,^\circ C$ ($R \neq Me$) or at $0\,^\circ C$ ($R = Me$). The copper(I) species were then ready for use.

RCu compounds. It was found that the 1-alkynylsilane $Ph_3SiC{\equiv}CH$ (Ia) undergoes a smooth, regio- and stereo-specific addition of RCu reagents when R is branched or unbranched alkyl but not when R is methyl. Protolysis of the intermediate adduct IIa (Scheme 1) gave 1-alkenylsilanes IIIa in excellent yields. The poor reactivity of MeCu towards alkylacetylenes is well known [2], and so its unreactivity towards Ia was not unexpected. Similar experiments with (trimethylsilyl)acetylene, $Me_3SiC{\equiv}CH$ (Ib), gave results that were satisfactory only when R in the reagents used was a branched alkyl group. The use of BuCu, for instance, gave a mixture of the desired adduct (80 rel. %), $BuCH{=}C(Bu)SiMe_3$ (18 rel. %) and the 1,3-diene $BuCH{=}C(SiMe_3)CH{=}CHSiMe_3$ (2 rel. %). The mono-ene contaminant arises by coupling of the intermediary vinylcopper(I) compound IIb with BuCu, and the diene by addition of adduct IIb to Ib (see below). The attempted addition of PhCu to Ia,Ib was unsuccessful.

The α-silyl substituted vinylcopper(I) compounds are fairly stable. Vinylcopper(I) compounds usually dimerize rapidly above $-10\,^\circ C$ [2], but solutions of our adducts can be stirred at room temperature during 1.5 h without detectable dimerization (as established for IIa). It could be that the dimerization is inhibited by steric hindrance from the silyl group.

The intermediate adducts shown in Scheme 1 react with a variety of electrophiles. Because of the pronounced thermal stability of the adducts, the presence of stabilizing agents like trimethylphosphite prior to the addition of the elelectrophile is not required. Thus, 1-halovinylsilanes were obtained by treating the intermediary adducts with *N*-chlorosuccinimide (E = Cl), *N*-bromosuccinimide or cyanogen bromide (E = Br), or iodine (E = I). When methyl methanethiolsulfonate, cyanogen chloride or trimethyltin chloride were added, vinylic silanes were formed bearing a MeS, NC or Me_3Sn group in the α-position. Allylation and methylation were carried out with allyl bromide and methyl iodide, respectively. For yields, physical constants and some ^1H NMR data for compounds III, see Table 1.

$R_2CuMgCl$ and R_3Cu_2MgCl compounds. Silane Ia reacted smoothly with dialkylcuprates, $R_2CuMgCl$, in which R is a linear or branched alkyl group. Protolysis of the intermediary adducts IVa afforded pure (*E*)-1-alkenylsilanes IIIa (Scheme 2).



SCHEME 1

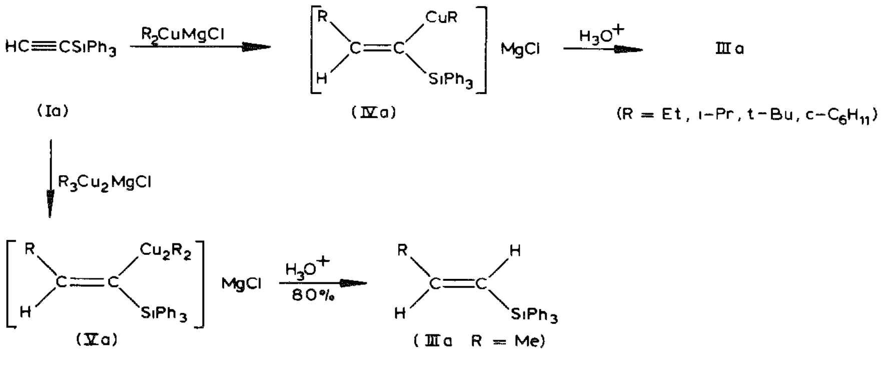
Only one of the two available groups R of the cuprate was transferred at an acceptable rate. Substantial differences in rate between transfer of the first and second group R from such cuprates have been observed in other cases [2,7]. The fact that one of the two available groups R is wasted makes the reaction less attractive than the RCu reaction. Nevertheless, the $R_2CuMgCl$ approach could be valuable where use of RCu is unsuccessful. It was shown (see above) that MeCu shows little tendency to add to Ia. We therefore attempted the conversion of Ia by $Me_2CuMgCl$ into the β-methyl-substituted vinylsilane, but the results were disappointing. Only minor amounts of the adduct were obtained, together with starting material and side-products. The $R_2CuMgCl$ approach in this case, therefore, does not offer any advantage over the RCu reaction. We then turned to the dicuprate Me_3Cu_2MgCl; it was recently shown that this compound is an excellent reagent for conversion of alkylacetylenes into vinylcuprates [8]. We found that silane Ia could be converted regio- and stereo-specifically into the desired adduct IIIa ($R = Me$, Scheme 2) by using an equimolar amount of Me_3Cu_2MgCl (yield of IIIa, $\simeq 70\%$)

The behaviour of silane Ib towards $R_2CuMgCl$ and R_3Cu_2MgCl was investigated for $R =$ n-butyl or isopropyl. Reaction of Ib with an equimolar amount of Bu_3Cu_2MgCl for 1.5 h at $-30\,^\circ C$ produced pure adduct Vb (Scheme 3), which on protolysis gave adduct IIIb ($R = Bu$) in 98% yield. Adduct IIIb ($R = Bu$) contained 7% of the 1,3-diene $BuCH{=}C(SiMe_3)CH{=}CHSiMe_3$ when it was prepared by treating Ib with 0.9 mol equivalent of Bu_2MgCl for 1.5 h at $0\,^\circ C$ (total yield of IIIb and 1,3-diene, 92%). The ratio IIIb/1,3-diene dropped to 50/50 when 7.0 mol equivalents of Ib were stirred with $Bu_2CuMgCl$ for 72 h at $20\,^\circ C$ (total yield of IIIb and 1,3-diene, 65% based on two available R groups). The interesting diene (compound VIIb in Scheme 3) was formed almost exclusively in the reaction of 7.0 mol equivalents of Ib with the dicuprate Bu_3Cu_2MgCl for 72 h at $20\,^\circ C$ (ratio IIIb/VIIb 4/96; total yield of IIIb and VIIb, 95% based on transfer of all three groups R); similar results were found using i-Pr_3Cu_2MgCl (ratio IIIb/VIIb 9/91; total yield of IIIb and VIIb, 91% based on transfer of all three groups R).

The 1,3-dienyl intermediates VIb reacted smoothly with the electrophiles methylmethanethiol sulfonate and allyl bromide to give compounds VIIb in which E is SMe and allyl, respectively. Details of the preparation of VIIb, their physical constants and some characteristic ^1H NMR data are given in Table 2.

It should be mentioned that suitable conditions have not yet been found for

(Continued on p. 322)



SCHEME 2

TABLE 1

PREPARATION, PHYSICAL CONSTANTS AND SPECTROSCOPIC DATA FOR ADDUCTS $RCH^1=C(E)SiR_3'$ (IIIa: R′ = Ph; IIIb: R′ = Me)

Starting compound	Copper(I)[a] reagent	Electrophile	Product[d]				B.p. (°C/mmHg)	n_D^{20}	M.p. (°C)	¹H NMR (CCl_4, Me_4Si)		
			III	R	E	Config.				δ(E)	δ(H¹)	³J(H¹,E)
Ia	Me_3Cu_2MgCl	H_3O^+	IIIa	Me	H	*E*[c]			80–82	6.25	6.22–5.87	16.8
Ia	EtCu[b]	H_3O^+	IIIa	Et	H	*E*			102–103	6.24	6.22	18.9
		NBS	IIIa	Et	Br	*Z*			79–80		6.77	
		I_2	IIIa	Et	I	*Z*			97–98		6.55	
Ia	i-PrCu[b]	H_3O^+	IIIa	i-Pr	H	*E*			84–85	6.20	6.15	18.3
		MeI	IIIa	i-Pr	Me	*E*			46–48	1.83	6.09	1.7
Ia	t-BuCu[b]	H_3O^+	IIIa	t-Bu	H	*E*			80–81	6.21	6.10	18.0
		NCS	IIIa	t-Bu	Cl	*Z*			84–85		6.43	
Ia	c-C_6H_{11}[b]	H_3O^+	IIIa	c-C_6H_{11}	H	*E*			52–53	6.20	6.10	18.0
Ib	Bu_3Cu_2MgCl	H_3O^+	IIIb	Bu	H	*E*	55–57/19	1.4277		5.96	5.62	18.8
Ib	i-PrCu	H_3O^+	IIIb	i-Pr	H	*E*	65–66/100	1.4187		5.94	5.47	18.0
		MeI	IIIb	i-Pr	Me	*E*	42–43/17	1.4219		1.63	5.50	1.5
		NCS	IIIb	i-Pr	Cl	*Z*	62–63/18	1.4438			5.72	
		BrCN	IIIb	i-Pr	Br	*Z*	70–72/19	1.4644			5.97	
		I_2	IIIb	i-Pr	I	*Z*	70–72/18	1.4960			5.80	
		$MeSO_2SMe$	IIIb	i-Pr	MeS	*Z*	72–74/19	1.4755		2.12	5.83	
		Me_3SnCl	IIIb	i-Pr	Me_3Sn	*Z*	90–92/20	1.4773		0.13	6.23	
Ib	t-BuCu	H_3O^+	IIIb	t-Bu	H	*E*	38–39/18	1.4220		5.97	5.48	19.4
		MeI	IIIb	t-Bu	Me	*E*	55–56/18	1.4365		1.96	5.62	1.5
		NCS	IIIb	t-Bu	Cl	*Z*	73–74/18	1.4406			5.86	
		NBS	IIIb	t-Bu	Br	*Z*	76–77/19	1.4678			6.28	
		I_2	IIIb	t-Bu	I	*Z*	44–45/0.6	1.4993			6.50	
		ClCN	IIIb	t-Bu	CN	*E*			49–50		6.33	
		C_3H_5Br[c]	IIIb	t-Bu	C_3H_5[c]	*E*	78–80/25	1.4524			5.68	
		$MeSO_2SMe$	IIIb	t-Bu	MeS	*Z*	70–72/20	1.4774		2.17	6.05	
		Me_3SnCl	IIIb	t-Bu	Me_3Sn	*Z*	110/20	1.4851		0.15	6.76	
Ib	c-C_6H_{11}	H_3O^+	IIIb	c-C_6H_{11}	H	*E*	95–96/25	1.4582		5.90	5.55	19.1

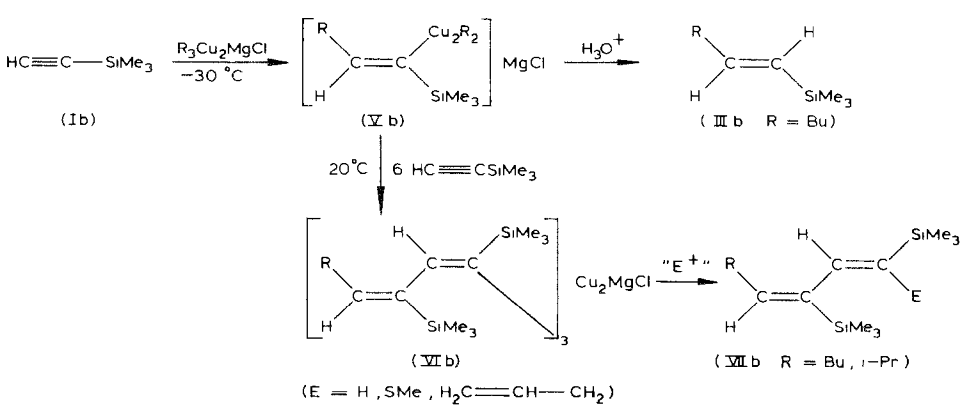
[a] Equimolar amounts of I and copper(I) reagent were used, unless otherwise stated. [b] Comparable results were obtained by using the corresponding cuprate, $R_2CuMgCl$ (one R transfer; studied for E = H). [c] $C_3H_5 = H_2C{=}CHCH_2$. [d] Yields, calculated on the cuprate assuming transfer of one group R, were over 90% unless otherwise stated. Purity of the products > 95% (based on ¹H NMR and GLC analysis). [e] Yield, 70% (based on transfer of one methyl group).

TABLE 2

PREPARATION, PHYSICAL CONSTANTS AND SPECTROSCOPIC DATA FOR 1,3-DIENES $R\overset{4}{C}H{=}\overset{3}{C}(SiMe_3)\overset{2}{C}H{=}\overset{1}{C}(E)SiMe_3$ (VIIb)

Copper(I)[a] reagent	Electrophile	Product VIIb			Yield[c] (%)	B.p. (°C/mmHg)	n_D^{20}	^1H NMR (CCl_4, Me_4Si)			
		R	E	Config. of $\Delta^{1,2}$ [b]				δ(E)	δ(H–C^2)	δ(H–C^4)	^3J(H–C^2,E)
Bu_3Cu_2MgCl	$H_3O^{\oplus}$	Bu	H	*E*	90	110-111/15	1.4653	5.66	6.82	5.75	19.1
	C_3H_5Br[d]	Bu	C_3H_5[d]	*E*	87	140-141/19	1.4717		6.21	5.71	
	$MeSO_2SMe$	Bu	SMe	*Z*	90	120-122/2	1.4885	2.10	6.31	5.56	
i-Pr_3Cu_2MgCl	$H_3O^{\oplus}$	i-Pr	H	*E*	80	95-97/19	1.4598	5.68	6.80	5.53	19.2
	$MeSO_2SMe$	i-Pr	SMe	*Z*	78	125-126/18	1.4854	2.12	6.46	5.42	

[a] 7.0 mol equiv. of silane Ib were used. [b] Configuration of $\Delta^{3,4}$ is assumed to be *E* in all cases, being based on protolysis of the initial intermediate Vb (studied for R = Bu). [c] Calculated on the cuprate and based on transfer of all groups R. Purity > 95%, as estimated from ^1H NMR and GLC analysis. [d] $C_3H_5 = H_2C{=}CHCH_2$.



SCHEME 3

satisfactory conversion of compounds such as $CH_3C{\equiv}SiR_3'$ into vinylic silanes by the routes described above. In this respect, the behaviour of such 1-alkynylsilanes resembles that of normal non-terminal alkynes [9].

Experimental

All reactions were performed under dry nitrogen. Tetrahydrofuran was distilled from $LiAlH_4$. Grignard reagents were prepared from the organic chloride in THF; their molarity was determined by Watson's titration method [10]. Lithium bromide was dried at 220 °C in high vacuum and was used as a 3.0 *M* solution in THF for the preparation of the cuprate $LiCuBr_2$ by mixing it with an equimolar amount of cuprous bromide. The 1-alkynylsilanes were made by the procedure described in ref. 11. ^1H NMR data for the products were determined on a Varian EM-390 spectrometer.

(a). Preparation of the organocopper(I) reagents. To a stirred homogeneous solution of $LiCuBr_2$ (0.01 or 0.02 mol) in THF (25 ml) was added a $\simeq$ 1.0 *M* THF solution of RMgCl (0.01 mol for the RCu reagents, 0.02 mol for the $R_2CuMgCl$ reagents, and 0.03 mol for the R_3Cu_2MgCl reagents), at 0 °C in the case of R = Me and at -60 °C in the other cases. The resulting mixture was stirred for 0.5 h at 0 and -60 °C, respectively, and the solution obtained was used as described below.

(b). Conversion of 1-alkynylsilanes into III. To the copper(I) reagent (0.01 mol, see under (a)) the 1-alkynylsilane I (0.01 mol) was added, at -60 °C. The mixture was then stirred for 24 h at 0 °C (conversion of Ia by Me_3Cu_2MgCl), for 1.5 h at 20 °C (conversion of Ia by RCu and $R_2CuMgCl$), for 1.5 h at 0 °C (conversion of Ib by RCu and $Bu_2CuMgCl$), or for 1.5 h at -30 °C (conversion of Ib by Bu_3Cu_2MgCl). Protolysis of the resulting adducts afforded compounds III with E = H. Introduction of the other groups E into III was carried out by adding 1.1 mol equivalent of the appropriate electrophile at -60 °C to the intermediate adduct. The mixture was stirred for 10 min at -60 °C, then the temperature of the mixture was allowed to rise during 30 min to 20 °C. Stirring at this temperature was continued for 30 min. Work-up was carried out by pouring the mixture into an aqueous solution of NH_4Cl containing NaCN (1 g). The product was extracted with pentane/ether (1/1 v/v). After washing and drying ($MgSO_4$) of the extract, the

solvent was stripped off. The residue was crystallized from methanol or distilled in vacuum (see Table 1). The purity of the compounds III obtained was at least 98% by GLC (SE 33 column).

(c). Conversion of 1-alkynylsilane Ib into VIIb. To the copper(I) reagent R_3Cu_2MgCl (0.01 mol, see under a) the 1-alkynylsilane Ib (0.07 mol) was added at −60 °C. The mixture was stirred for 72 h at 20 °C. Reaction of the intermediate adduct with electrophiles and work up was carried out as described for IIIb. Distillation of the crude products at reduced pressure gave compounds VIIb, with a purity of at least 98% by GLC (SE 33 column). Physical constants and other data for VIIb are shown in Table 2.

Acknowledgement

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