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Preliminary communication

CHEMISTRY OF ORGANOSILICON COMPOUNDS

CXXV. A NOVEL METHOD OF PREPARING ACYLSILANES FROM α-SILOXYALLYLSILANES BY TRANSITION METAL CATALYZED ISOMERIZATION OF DOUBLE BONDS

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Summary

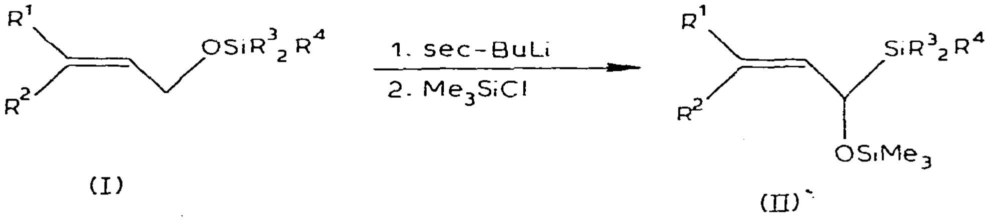
Nine α-siloxyallylsilanes were prepared regiospecifically by silylation of metalated alkyl-substituted allyloxysilanes with chlorosilanes in good yield. These compounds were converted readily to acylsilanes by transition metal-catalyzed isomerization of double bonds under neutral conditions.

Acylsilanes, introduced first by Brook [1], are an interesting class of compounds because of their peculiar spectroscopic and chemical behavior, and numerous reports on the preparation and reactions of acylsilanes have been published [2,3]. However, the reported methods of preparation of acylsilanes, especially of aliphatic acylsilanes are not always satisfactory, because of the inaccessibility of the starting materials, the inapplicability to acylsilanes in general, and the occurrence of side reactions. We report here a novel and convenient method of preparing aliphatic acylsilanes by the transition metal-catalyzed isomerization of α-siloxyallylsilanes.

We have previously demonstrated that α-siloxyallylsilanes (II, $R^1 = R^2 = H$) can be prepared regiospecifically in good yield by the reaction of a chlorosilane with a carbanion derived from an allyloxysilane (I, $R^1 = R^2 = H$) by metalation with sec-butyllithium in THF/HMPA [4]. During the course of further studies, we have found that (α-trimethylsiloxy)allylsilanes can be prepared from alkyl-substituted allyloxysilanes by a similar procedure (Table 1).

1,2-Diallyloxytetramethyldisilane gave 1-(α-trimethylsiloxyallyl)-2-sec-butyltetramethyldisilane instead of the expected bis(α-siloxyallyl)disilane.

The α-siloxyallylsilanes thus obtained were heated at reflux in methanol and/or water in the presence of a catalytic amount of 10% palladium on carbon



(1)

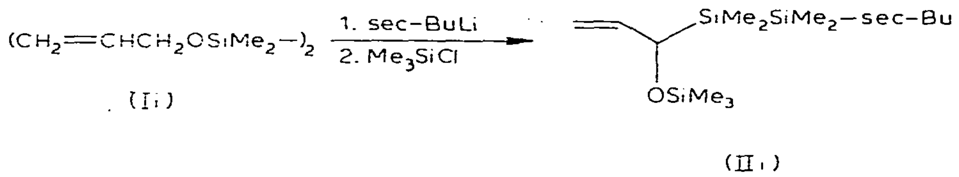
a $R^1 = R^2 = H ; R^3 = R^4 = Me$
b $R^1 = R^2 = H ; R^3 = R^4 = Et$
c $R^1 = R^3 = R^4 = Me ; R^2 = H$
d $R^1 = Me ; R^2 = H ; R^3 = R^4 = Et$
e $R^1 = n\text{-}Pr ; R^2 = H ; R^3 = R^4 = Me$
f $R^1 = i\text{-}Pr ; R^2 = H ; R^3 = R^4 = Me$
g $R^1 = R^2 = H ; R^3 = Me\ R^4 = SiMe_3$
h $R^1 = R^2 = R^3 = R^4 = Me$

TABLE 1

REACTIONS OF METALATED ALLYLOXYSILANES WITH TRIMETHYLCHLOROSILANE

Entry	Allyl silyl ether	Product	Yield (%)		B.p. (°C/mmHg)
1	$CH_2{=}CHCH_2OSiMe_3$	$CH_2{=}CH\underset{\underset{OSiMe_3}{\vert}}{C}HSiMe_3$	IIa	(84)	62/35
2	$CH_2{=}CHCH_2OSiEt_3$	$CH_2{=}CH\underset{\underset{OSiMe_3}{\vert}}{C}HSiEt_3$	IIb	(92)	85/9
3	$CH_3CH{=}CHCH_2OSiMe_3$	$CH_3CH{=}CH\underset{\underset{OSiMe_3}{\vert}}{C}HSiMe_3$	IIc	(50)	86/40
4	$CH_3CH{=}CHCH_2OSiEt_3$	$CH_3CH{=}CH\underset{\underset{OSiMe_3}{\vert}}{C}HSiEt_3$	IId	(90)	68—71/2
5	$CH_3(CH_2)_2CH{=}CHCH_2OSiMe_3$	$CH_3(CH_2)_2CH{=}CH\underset{\underset{OSiMe_3}{\vert}}{C}HSiMe_3$	IIe	(57)	94—99/15
6	$(CH_3)_2CHCH{=}CHCH_2OSiMe_3$	$(CH_3)_2CHCH{=}CH\underset{\underset{OSiMe_3}{\vert}}{C}HSiMe_3$	IIf	(65)	80—81/15
7	$CH_2{=}CHCH_2OSiMe_2SiMe_3$	$CH_2{=}CH\underset{\underset{OSiMe_3}{\vert}}{C}HSiMe_2SiMe_3$	IIg	(81)	97—98/15
8	$(CH_3)_2C{=}CHCH_2OSiMe_3$	$(CH_3)_2C{=}CH\underset{\underset{OSiMe_3}{\vert}}{C}HSiMe_3$	IIh	(27)	40/6
9[a]	$(CH_2{=}CHCH_2OSiMe_2)_2$	$CH_2{=}CH\underset{\underset{OSiMe_3}{\vert}}{C}HSiMe_2SiMe_2\text{-sec-Bu}$	IIi	(62)	78—80/5

[a] Two equivalents of sec-butyllithium were used.



(2)

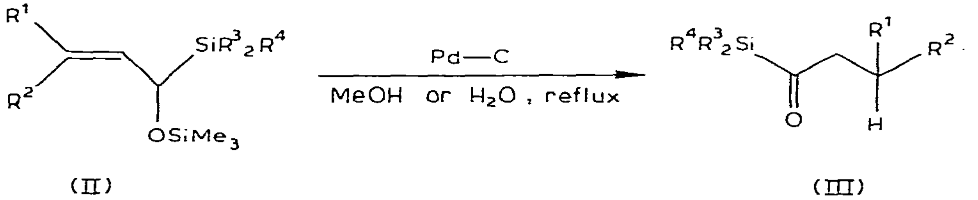
to give the corresponding acylsilanes (III) in moderately high yield. The results are presented in Table 2*.

TABLE 2

DOUBLE BOND ISOMERIZATIONS OF α-SILOXYALLYLSILANES IN THE PRESENCE OF 10% PALLADIUM ON CARBON [a]

Entry	α-Siloxyallylsilanes	Solvent	Reaction time (h)	Product	Yield (%) [b]
1	IIa	MeOH	12	$Me_3SiCOCH_2CH_3$ [7]	80 [c]
2	IIb	MeOH	7.5	$Et_3SiCOCH_2CH_3$	81 (79) [d]
3	IIc	H_2O	60	$Me_3SiCO(CH_2)_2CH_3$ [8]	62 [d]
4	IId	H_2O	24	$Et_3SiCO(CH_2)_2CH_3$	59
5	IId	20% H_2O/MeOH	84	$Et_3SiCO(CH_2)_2CH_3$	65
6	IIe	H_2O	12	$Me_3SiCO(CH_2)_4CH_3$ [9]	51
7	IIf	H_2O	24	$Me_3SiCO(CH_2)_2CH(CH_3)_2$	66
8	IIg	MeOH	24	$Me_3SiSiMe_2COCH_2CH_3$	59
9	IIi	MeOH	12	sec-BuMe$_2$SiSiMe$_2$COCH$_2$CH$_3$	60

[a] All reactions were carried out at reflux temperature. [b] Yields after isolation by TLC unless otherwise noted. [c] Determined by GLC. [d] Yields after isolation by distillation.



(3)

As shown in the Table, all compounds II except for IIh smoothly undergo olefinic bond isomerization [5] to give compounds III generally in good yield (50—80%). Introduction of a substituent into the γ-position decreased the yield of III and appreciable amounts of the corresponding carbinol, a hydrolysis product of II, were recovered. The reaction of IIh gave 3-hydroxy-3-methylbut-1-enyltrimethylsilane in 88% yield.

Proper combination of a solvent and a transition metal catalyst is crucial for the isomerization reaction, the reaction catalyzed by palladium on carbon in methanol and/or water giving the most satisfactory results among various combinations of solvents and transition metal catalysts such as $Pd(OAc)_2$, $PdCl_2(PhCN)_2$,

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*All new compounds obtained in this work gave correct elemental analyses and spectral data.

$RhCl(CO)(PPh_3)_2$, $RhH(CO)(PPh_3)_3$, and $RhCl(PPh_3)_3$ in benzene, THF, dioxane, methanol, and water.

It is probable that the reaction proceeds through the hydrolysis products of II, α-hydroxyallylsilanes. Indeed, the corresponding α-hydroxyallylsilane, independently prepared by prior hydrolysis of II, similarly undergoes isomerization to give the acylsilane (III) under these conditions. Isomerization of allyl alcohols to carbonyl compounds has been reported [5].

From a mechanistic aspect, it is interesting to note that alkyldisilanyl ethyl ketones were also obtained in good yield in the present reaction, because a silicon—silicon σ bond of vinylpolysilanes is readily cleaved in a protic solvent in the presence of a transition metal catalyst [6]. In this way, two new acyldisilanes are prepared. The λ_{max} (nm) and ϵ were: $Me_3SiSiMe_2COCH_2CH_3$ 351(251), 365(394), 380(363); sec-$BuMe_2SiSiMe_2COCH_2CH_3$ 351(218), 364(341), 380(322).

A representative conversion from II to III is accomplished as follows:

In a 50 ml flask, an α-siloxyallylsilane (II) (1.0 mmol) and 10% palladium on carbon (20 mg) were placed in dry methanol (5 ml) and the reaction mixture was heated at reflux with stirring in an oil bath (80—90°C) for a given period of time. After disappearance of the starting material II was confirmed by GLC, the reaction mixture was passed through a short column (2 cm) packed with silica gel and concentrated under reduced pressure. The residue was purified by either distillation or preparative TLC.

Acknowledgment.

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References

1 A.G. Brook, J. Amer. Chem. Soc., 79 (1957) 4373.
2 For a review, see A.G. Brook, Advan. Organometal. Chem., 7 (1968) 95.
3 For recent developments, see (a) A.G. Brook and J.W. Harris, J. Amer. Chem. Soc., 98 (1976) 3382; (b) T. Sato, M. Arai and I. Kuwajima, ibid., 99 (1977) 5827, and ref. cited therein.
4 A. Hosomi, H. Hashimoto and H. Sakurai, J. Org. Chem., 43 (1978) 2551.
5 (a) A.J. Birch and I.D. Jenkins, in H. Alper (Ed.), Transition Metal Organometallics in Organic Synthesis, Vol. 1, Academic Press, New York, 1976, p. 49; (b) P.M. Maitlis, The Organic Chemistry of Palladium, Vol. II, Academic Press, New York, 1971, p. 128; (c) W. Keim, in G.N. Schrauzer (Ed.), Transition Metals in Homogeneous Catalysis, Marcel Dekker, New York, 1971, p. 81; (d) R.F. Heck, Organotransition Metal Chemistry, Academic Press, New York, 1974, p. 76.
6 K. Yamamoto, M. Kumada, I. Nakajima, K. Maeda and N. Imaki, J. Organometal. Chem., 13 (1968) 329.
7 A.G. Brook, P.J. Dillon and P. Pearce, Can. J. Chem., 49 (1971) 133.
8 P. Bourgeois, J. Dunoguès and N. Duffaut, J. Organometal. Chem., 80 (1974) C25.
9 I. Kuwajima, M. Arai and T. Sato, J. Amer. Chem. Soc., 99 (1977) 4181.